Master's Thesis
Hydrogeology and Environmental Geology

ARSENIC SPECIATION AND CONCENTRATIONS IN MINING-IMPACTED WATERS IN FINLAND

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2019

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Tiedekunta – Fakultet – Faculty	Koulutusohjelma – Utbildingsprogram – Degree Programme
Faculty of Science	Master's Programme in Geology and Geophysics

Tekijä – Författare – Author

Toni Hekkala

Työn nimi – Arbetets titel – Title

Arsenic speciation and concentrations in mining-impacted waters in Finland

Opintosuunta – Studieinriktning – Study track

Hydrogeology and Environmental Geology

Työn laji – Arbetets art – Level	Aika – Datum – Month and year	Sivumäärä – Sidoantal – Number of pages
Master's Thesis	October 2019	57 p. + 4 Appendices

Tiivistelmä – Referat – Abstract

Arsenic (As) is a metalloid naturally present in the environment. Arsenic species vary in toxicity. Metal mining has contributed to the anthropogenic input of arsenic to groundwaters and surface waters. In this study, water samples were collected from 20 sample points in three mining-impacted study areas in Finland: the former Ylöjärvi Cu–W–As and Haveri Au–Cu mines, and the active Pyhäsalmi Zn–Cu mine. Six groundwater well samples, eleven surface water samples and three tailings seepage collection ditch samples were analyzed for dissolved arsenic speciation by HPLC-ICP-MS and for geochemical composition by ICP-MS, titration, and ion chromatography.

Dissolved arsenic concentrations ranged from 14.2 to 6649 µg L^{-1} in samples collected at the Ylöjärvi study area, from 0.5 to 6.2 µg L^{-1} in samples collected at the Haveri study area, and from 0.2 to 9.4 µg L^{-1} in samples collected at the Pyhäsalmi study area. In all study areas, measured dissolved arsenic concentrations showed a general decrease from the tailings to the surroundings. Speciation analysis showed that two of the samples collected at the Ylöjärvi study area had arsenite [As(III)] as the dominant form of dissolved inorganic arsenic (iAs), three had arsenate [As(V)] as the dominant form of dissolved iAs, and four had a mixture of both. In the water samples collected at the Haveri and Pyhäsalmi study areas, all concentrations of dissolved arsenic species were below method detection limits. Also, none of the 22 water samples analyzed for arsenic speciation had dissolved MMA or DMA concentrations above method detection limits. Identification of dissolved arsenic species in the sampled waters in Haveri and Pyhäsalmi, and of MMA and DMA in all sampled waters requires more detailed study.

A significant 2-tailed Pearson correlation between dissolved arsenic and dissolved molybdenum (Mo) (r=0.80**, n=20), and dissolved arsenic and dissolved potassium (K) (0.68**, n=19) suggests that in these three study areas the distributions of dissolved arsenic and Mo, as well as dissolved arsenic and K may be controlled by the same environmental variables. Anomalously high maximum concentrations of dissolved Al, Ca, Co, Cu, Fe, Ni, and SO_4 were measured in surface water samples collected at the Ylöjärvi and Haveri study areas, and in a seepage collection ditch sample collected at the Pyhäsalmi study area.

Avainsanat – Nyckelord – Keywords

Arsenic, dissolved, speciation, species, geochemical, geochemistry, mine, mining, tailings

Ohjaaja tai ohjaajat – Handledare – Supervisor or supervisors

Juhani Virkanen and Seija Kultti

Säilytyspaikka – Förvaringställe – Where deposited

Muita tietoja – Övriga uppgifter – Additional information

25 figures, 6 tables

Tiedekunta – Fakultet – Faculty	Koulutusohjelma – Utbildingsprogram – Degree Programme
Matemaattis-luonnontieteellinen	Geologian ja geofysiikan maisteriohjelma

Tekijä – Författare – Author

Toni Hekkala

Työn nimi – Arbetets titel – Title

Arsenic speciation and concentrations in mining-impacted waters in Finland

Opintosuunta – Studieinriktning – Study track

Hydrogeologia ja ympäristögeologia

Työn laji – Arbetets art – Level	Aika – Datum – Month and year	Sivumäärä – Sidoantal – Number of pages
Maisterintutkielma	Lokakuu 2019	57 s. + 4 Liitettä

Tiivistelmä – Referat – Abstract

Arseeni (As) on elinympäristössämme luonnostaan esiintyvä puolimetalli. Useilla arseenin yhdisteillä, kuten epäorgaanisilla arseniittiyhdisteillä [As(III), $H_nAsO_3^{3-n}$], on myrkyllisiä ja karsinogeenisia ominaisuuksia. Sulfidimalmeja hyödyntävä kaivostoiminta voi nostaa arseenin pitoisuuksia kaivosalueen pinta- ja pohjavedessä. Tässä tutkielmassa kerättiin yhteensä 18 pohjavesinäytettä, 45 pintavesinäytettä ja yhdeksän suotoveden keräysojan vesinäytettä 20:stä kaivosvaikutteisesta näytepisteestä, jotka sijaitsivat Ylöjärven suljetun Cu–W–As-kaivoksen tutkimusalueella, Haverin suljetun Au–Cu-kaivoksen tutkimusalueella, sekä Pyhäsalmen Zn–Cu-kaivoksen tutkimusalueella. Vesinäytteistä analysoitiin liukoinen arseenin spesiaatio HPLC-ICP-MS-tekniikalla ja geokemiallinen koostumus ICP-MS:llä, pääionit ionikromatografialla ja alkaliteetti titraamalla. HPLC-ICP-MS:ää käytetään yleisesti nestemäisten arseenia sisältävien näytteiden spesiaatiotutkimuksessa.

Mitatut liukoisen arseenin pitoisuudet vaihtelivat Ylöjärven tutkimusalueen vesinäytteissä välillä 14,2–6649 µg L^{-1}, Haverin tutkimusalueen vesinäytteissä välillä 0,5–6,2 µg L^{-1}, ja Pyhäsalmen tutkimusalueen vesinäytteissä välillä 0,2–9,4 µg L^{-1}. Mitatut liukoisen arseenin pitoisuudet pienenivät kaikilla tutkimusalueilla etäisyyden kasvaessa rikastushiekka-alueelta pois päin. Arseenin spesiaatioanalyysi osoitti, että Ylöjärven tutkimusalueella kahdessa vesinäytteessä arseniitti [As(III)] oli vallitseva liukoisen epäorgaanisen arseenin (iAs) spesies, kolmessa näytteessä arsenaatti [As(V)] oli vallitseva iAs-spesies, ja neljässä näytteessä oli sekoitus molempia. Haverin ja Pyhäsalmen tutkimusalueiden vesinäytteissä liukoiset arseenin spesiekset eivät ylittäneet määritysrajoja. Kaikissa vesinäytteissä eri tutkimusalueilta liukoiset MMA- ja DMA-pitoisuudet olivat alle määritysrajojen. Tarkempi liukoisten arseenin spesiesten tunnistaminen Pyhäsalmen ja Haverin tutkimusalueilla tutkituista vesistä, sekä MMA:n ja DMA:n pitoisuuksien tunnistaminen kaikista tutkituista vesistä vaatii uusia tutkimuksia.

Liukoisen arseenin ja molybdeenin (Mo) pitoisuuksien merkitsevä korrelaatiokerroin oli 0,80** (n=20), ja lisäksi liukoisen arseenin ja kaliumin (K) pitoisuuksien merkitsevä korrelaatiokerroin oli 0,68** (n=19), mistä päätellen liukoisen arseenin ja Mo:n, sekä liukoisen arseenin ja K:n pitoisuudet tutkituilla alueilla voivat määräytyä samojen ympäristön muuttujien perusteella. Poikkeavan korkeita liukoisen Al:n, Ca:n, Co:n, Cu:n, Fe:n, Ni:n ja SO_4:n maksimipitoisuuksia mitattiin pintavesinäytteistä Ylöjärven ja Haverin tutkimusalueilla, sekä rikastushiekan suotoveden keräysojan vesinäytteestä Pyhäsalmen tutkimusalueella.

Avainsanat – Nyckelord – Keywords

Arseeni, spesiaatio, geokemia, kaivosteollisuus, ympäristövaikutukset, As(III), As(V)

Ohjaaja tai ohjaajat – Handledare – Supervisor or supervisors

Juhani Virkanen ja Seija Kultti

Säilytyspaikka – Förvaringställe – Where deposited

Muita tietoja – Övriga uppgifter – Additional information

25 kuvaa, 6 taulukkoa

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1. INTRODUCTION

1.1. Arsenic occurrence and mobility

Arsenic is a naturally occurring minor terrestrial element that exists ubiquitously in groundwater and surface water in both organic and inorganic forms. The chemical behavior of arsenic and its species in natural aquatic reservoirs has been studied extensively for the last decades because of its well-known human-health issues and toxicity to living organisms. There is sufficient evidence that long-term arsenic exposure can cause, for example, cancer of the large intestine, lung, kidney, and bone, and non-cancer diseases such as cardiovascular disorders and skin lesions (Enterline et al. 1995, National Research Council 2001, International Agency for Research on Cancer IARC 2012, Karagas et al. 2015).

Elevated levels of arsenic are present in groundwater worldwide. Arsenic is a geogenic problem in groundwater particularly in Bengal (e.g., Nickson et al. 2000, Pal et al. 2002, Chakraborti et al. 2016), but also elsewhere in Southeast Asia (e.g., Chen et al. 1994, Berg et al. 2001, Pham et al. 2017), and, e.g., Mexico (Rodriguez et al. 2004), Argentina (Bundschuh et al. 2004), Chile (Smith et al. 1998a), Hungary (Varsányi et al. 2006), Romania (Gurzau et al. 2001), and in parts of the USA (Bissen and Frimmel 2003). Since 1993, the World Health Organization has recommended a maximum contaminant level (MCL) of 10 µg L^{-1} for arsenic in drinking water, meant to be protective of human health (National Research Council 1999, World Health Organization 2017). In Finland, the Ministry of Social Affairs set the MCL for arsenic to 10 µg L^{-1} in drinking water and household water in 1994 (Finnish Ministry of Social Affairs and Health FMSAH 1994, FMSAH 2015).

In Finland, arsenic concentrations in groundwater and surface water are generally low. Backman and Lahermo (2004) reported 0.8% of water samples from springs and captured springs, 0.4% of water samples from dug ring-wells, and 12.2% of water samples from drilled bedrock wells having >10 µg L^{-1} arsenic. As seen in Table 1, in Finland, dug ring-

wells, springs and captured springs typically have lower arsenic concentrations than drilled bedrock wells (Backman and Lahermo 2004).

Table 1. A statistical summary of arsenic concentrations in Finland (in µg L^{-1}) in spring water samples, dug ring-well samples, and drilled bedrock well samples. Modified from Backman and Lahermo (2004).

	n	Median	Mean	Maximum	S.D.
Springs, captured springs	741	0.10	0.58	36.2	2.81
Dug ring-wells	1721	0.20	0.52	45	1.96
Drilled bedrock wells	2229	0.61	17.7	2230	117

S.D. = standard deviation

Arsenic can be mobile in a wide range of pH conditions, including highly acidic conditions of acid rock drainage (Bowell et al. 2014), while pH itself is a key factor in controlling arsenic sorption (Campbell and Nordstrom 2014). In many soil environments, arsenic transport is mainly controlled by adsorption or desorption (Smith et al. 1998b). Oxides, especially Fe oxides, have a strong adsorption affinity for arsenic under oxidizing, neutral to slightly acidic conditions (Smedley and Kinniburgh 2002). Particularly under oxidizing conditions, arsenic bound to Fe oxides is relatively immobile (Smedley and Kinniburgh 2002).

Metal mining and arsenic-bearing mineral processing have contributed to the global anthropogenic input of arsenic to groundwater and surface water. When sulfide minerals or arsenic-bearing ore, such as, e.g., pyrite (FeS_2), arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), or galena (PbS), that were once formed in reducing conditions, are exposed through mining and mineral processing to an oxidizing environment, a series of complex chemical weathering reactions are initiated. Oxidized sulfide minerals, especially in tailings environments, can produce acid rock drainage containing elevated levels of sulfate and hydrogen ions, and metals, such as arsenic (Lottermoser 2010, Nordstrom et al. 2015). For example, arsenopyrite, the most common arsenic-bearing mineral, found in a range of ore deposits, oxidizes during weathering to release arsenic and other constituents into solution.

Yunmei et al. (2007) showed that dissolved O_2 and Fe(III), important aqueous species in acid rock drainage (ARD) environments (Corkhill and Vaughan 2009), determine the

oxidation rate of arsenopyrite. O_2 and Fe(III) react with arsenopyrite with the generalized equations (after Walker et al. 2006 and Yunmei et al. 2007):

$$4FeAsS + 11O_2 + 6H_2O \rightarrow 4Fe^{2+} + 4H_3As(III)O_3 + 4SO_4^{2-} \qquad (1)$$

$$FeAsS + 7H_2O + 11Fe^{3+} \rightarrow 12Fe^{2+} + H_3As(III)O_3 + SO_4^{2-} + 11H^+ \qquad (2)$$

The reaction in Equation 1 does not generate acidity, but the reaction in Equation 2 does. However, the actual pH depends on the extent of secondary reactions, controlled by site-specific conditions (Walker et al. 2006).

1.2. Arsenic speciation

Chemical speciation of arsenic is fundamental in understanding the behavior, mobility and toxicity of arsenic. While there is a vast amount of documented research focusing both globally and locally on the distribution and concentrations of arsenic in natural and industrial aquatic systems, scientific data on arsenic speciation in such systems is more limited.

Arsenic is stable in five oxidation states (-III, -I, 0, +III, +V), but exists in groundwater and surface water mainly in two oxidation states: +III, and +V. The greatest risk of toxic exposure is associated with inorganic arsenic (iAs) (Mitchell 2014), the most toxic common form of which is trivalent arsenite [As(III), $H_nAsO_3^{3-n}$], followed by pentavalent arsenate [As(V), $H_nAsO_4^{3-n}$]. These are the two dominant species of arsenic in natural waters and soils (Cullen and Reimer 1989, Smith et al. 1998b, Hughes et al. 2011). Arsenic speciation, mainly controlled by Eh and pH (Smedley and Kinniburgh 2002), determines its behavior and mobility (Campbell and Nordstrom 2014), and also, how arsenic is metabolized (Mitchell 2014); trivalent arsenic is resorbed faster in biological systems than pentavalent arsenic (Bissen and Frimmel 2003). Monomethylated and dimethylated arsenicals (MMAs and DMAs) are methylated metabolites of arsenic that are often analyzed in arsenic speciation analysis along with As(III) and As(V). MMA(III) and DMA(III) have been shown to be toxicologically potent at high levels of exposure (Petrick et al. 2000, Mitchell 2014, Tchounwou et al. 2019).

In the reactions in Equations 1 and 2, As(III) is present as the uncharged ion H_3AsO_3, which can, at near-neutral pH, be oxidized to As(V) via the following reactions (after Walker et al. 2006):

$$2H_3As(III)O_3 + O_2 = 2HAs(V)O_4^{2-} + 4H^+ \qquad (3)$$

$$2H_3As(III)O_3 + O_2 = 2H_2As(V)O_4^{-} + 2H^+ \qquad (4)$$

As previously mentioned, arsenic sorption behavior is mainly controlled by pH. Adsorption studies on Fe oxides have shown that As(V) adsorption increases with decreasing pH, reaching maximum adsorption under low pH conditions, whereas As(III) adsorption does not increase with decreasing pH, instead, As(III) has a broad maximum adsorption around a pH of 7–9 (Dixit and Hering 2003, Campbell and Nordstrom 2014). In a study by Lafferty and Loeppert (2005), MMA(III) and DMA(III) were not significantly absorbed by goethite or ferrihydrite within a pH range of 3 to 11, even though As(III) was strongly adsorbed. Both As(III) and As(V) can form metal-arsenic complexes, of which iron-arsenic complexes can be important in acid rock drainage conditions of low pH and high Fe concentration (Campbell and Nordstrom 2014).

The occurrence of arsenic species in surface water and groundwater have been studied worldwide locally and also for large areas, e.g., Sorg et al. (2014) studied arsenic speciation in drinking water wells scattered across the USA. In Finland, the occurrence of arsenic species has been studied locally, e.g., Backman et al. (2006) and Backman et al. (2007) studied geogenic arsenic in drilled well waters in Pirkanmaa, SW Finland; and in anthropogenically contaminated sites, e.g., Carlson et al. (2002) studied arsenic occurrence and speciation in waters in the former Ylöjärvi Cu–W–As mine, which is included as a test site in this study. Results of these previous studies are compared with arsenic concentrations and speciation results of this study.

This study aims to investigate the occurrence or dissolved arsenic and its species, especially As(III) and As(V), in mining-impacted groundwater, surface water, and other aqueous pathways in tailings environments in the selected study areas in Finland.

Geochemical and physicochemical data are analyzed with respect to the occurrence of dissolved arsenic in different mining-impacted waters.

2. STUDY AREAS

Three study areas were selected to represent a range in mining activity and geological settings, based on three factors: (1) estimates of local arsenic occurrence based on previous research by Carlson et al. (2002), Parviainen (2009), Parviainen et al. (2012), Valo (2012), and Räisänen and Skinnari (2015), reporting arsenic concentrations sufficient for speciation analysis; (2) a sufficient number of possible sampling locations with regard to flow paths; and (3) logistics.

Figure 1. Locations of the study areas in Finland depicted as hollow circles on the map of Northern Europe.

The selected study areas include the abandoned Ylöjärvi Cu–W–As and Haveri Au–Cu mines, and the active Pyhäsalmi Zn–Cu mine in Pyhäjärvi (Fig. 1). All three study areas, located within the tectonic Western Finland Subprovince, are dominated by tailings environments and widely occurring Quaternary glacial and/or glaciolacustrine deposits.

2.1. Ylöjärvi, Pirkanmaa, Finland

Located 7 km NW of Ylöjärvi town center in Pirkanmaa, the former Ylöjärvi Cu–W–As mine operated in the area from 1943 to 1966 mining a total of about 4 Mt of ore, 2.8 Mt of which was deposited at the study area as tailings, including 1.1 Mt into tunnels (Carlson et al. 2002, Tornivaara et al. 2018). The former mining area is currently the property of the Finnish Forest and Park Service and is a restricted military area.

The main source of arsenic in the mining-impacted waters at the Ylöjärvi study area is the large tailings pile, which contains arsenic-bearing sulfide minerals (Parviainen et al. 2012): the host rock mined was a tourmaline breccia, occurring in the area as two subvertical zones about 150 m apart, with the most important minerals exploited being sulfides arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), and pyrrhotite ($Fe_{1-x}S$) (Himmi et al. 1979, Carlson et al. 2002). Exploiting deposits in the Paleoproterozoic Tampere Schist Belt, the former mine produced 2100 tonnes of arsenopyrite concentrate, and 567 tonnes of arsenic (Himmi et al. 1979). The large tailings pile, in the vicinity of which most samples were taken (Fig. 2), is on average 9.3 m thick, and has a maximum thickness of 16 m measured in 1981 (Carlson et al. 2002), and an area of about 15 ha. Parviainen et al. (2012) reported an average arsenic concentration of 2615 mg kg^{-1} in sequential extractions of the large tailings pile.

The grain size of the tailings is mainly that of silt, and partly fine to medium sand (Parviainen et al. 2012). As sulfide minerals in the tailings pile have been exposed to an oxidizing environment, it is possible that, e.g., precipitated iron has formed impermeable and dense layers of soil inside the tailings.

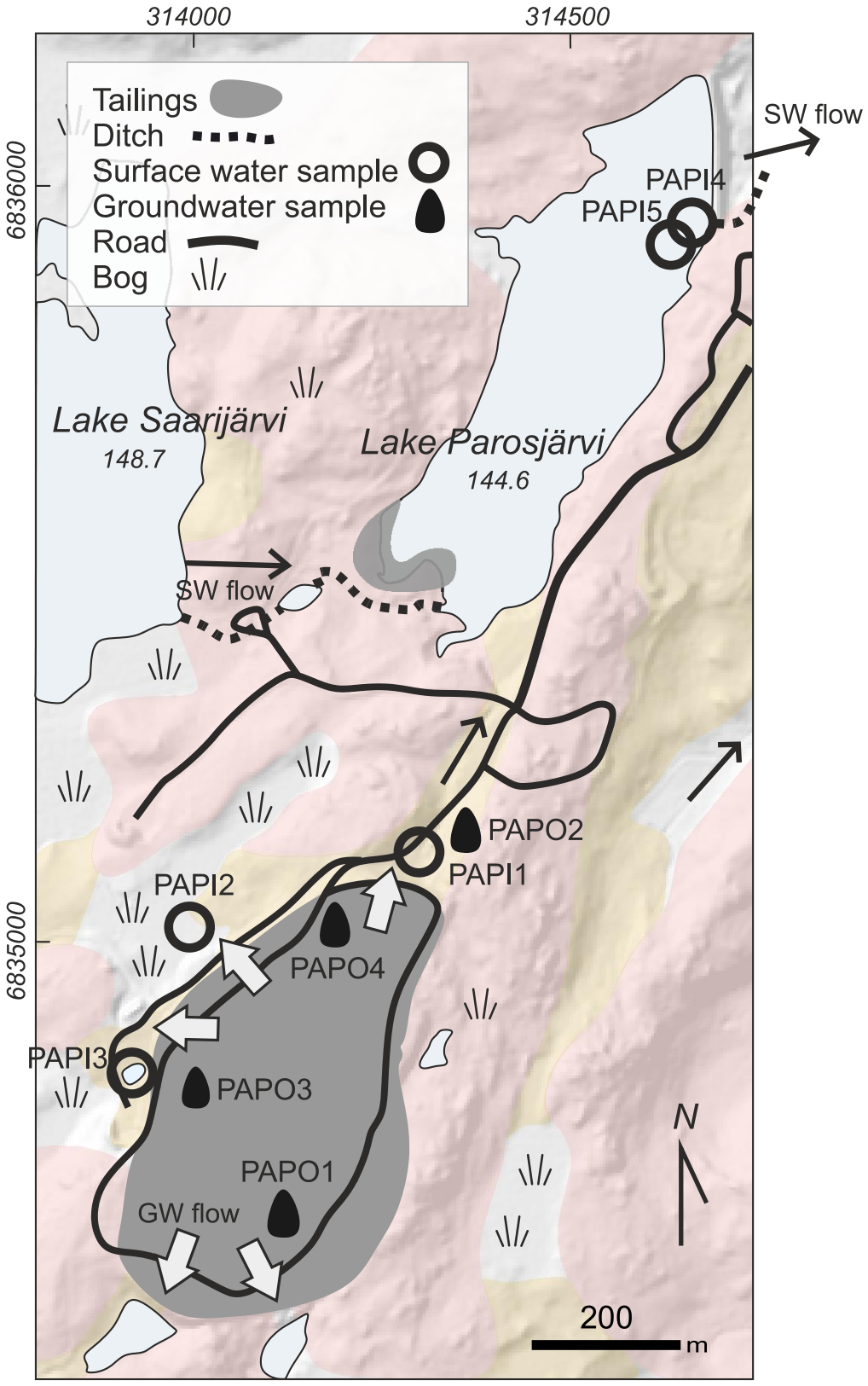

Figure 2. Generalized map of the Ylöjärvi study area. Surface water flow directions (modified from Parviainen et al. 2012 and National Land Survey of Finland 2019) are depicted as black arrows, groundwater flow directions (modified from Carlson et al. 2002) are depicted as white arrows. Red color represents exposed bedrock and areas with a thin cover (<1 m) of Quaternary deposits, brown color represents sandy till deposits (modified from Carlson et al. 2002). Hillshade data is modified from National Land Survey of Finland (2019). The areal extents of the tailings deposits were modified from Carlson et al. (2002), Parviainen et al. (2012) and National Land Survey of Finland (2019).

The surface of the large tailings pile is approximately 9 m above surrounding ground level (Parviainen 2012). Carlson et al. (2002) found the tailings pile to be thickest in the SE and NW parts of the tailings with thicknesses of 14.5–16 m and 13.3 m, respectively. At the large tailings pile, groundwater level follows the topography, and lies some meters higher than in the areas surrounding the large tailings pile (Carlson et al. 2002). Groundwater seepage, transporting contaminants to the surroundings, can be observed in all directions outside the edge of the large tailings pile (Carlson et al. 2002), in areas where, e.g., the edge of the tailings lies on top of a layer consisting of more impermeable material. Carlson et al. (2002) reported that the wetland outside the NW edge of the tailings is severely contaminated because of tailings groundwater seepage. As can be seen in Figure 2, in this study, the sample PAPI2 was collected at the contaminated wetland.

At the study area, the natural soil is mostly sandy till, but also peat. Bedrock outcrops are common. Stretching from the southeastern edge of the large tailings pile to the northeastern shore of Lake Parosjärvi, there is a NE-SW-aligned zone of bedrock above surrounding ground level, controlling surface water and groundwater flow. Surface water in the study area drains mainly to Lake Parosjärvi (0.145 km^2). Water from Lake Saarijärvi also drains to Lake Parosjärvi. Then, from the NE part of Lake Parosjärvi, water flows about 8 km east to Lake Näsijärvi (255 km^2) through Parosjärvenoja stream and Lake Vähävahantajärvi. There are no classified aquifers inside the study area according to the nation-wide groundwater database POVET (Finnish Environment Institute 2019).

Figure 3. Groundwater well sampling point PAPO1 located in the southern part of the tailings. Photo taken facing north.

In the Ylöjärvi study area, groundwater well samples were collected from four wells installed in 2002 (Carlson et al. 2002). The groundwater wells from which the samples PAPO1 (Fig. 3), PAPO3, and PAPO4 were taken, are located in the large tailings pile (Fig. 2). It is important to note that the measurements are not necessarily representative of the groundwater below the surface of the Ylöjärvi tailings.

Figure 4. Surface water sampling point PAPI3 located outside the western edge of the tailings.

Surface water samples were collected from five locations, including two from northern Lake Parosjärvi, and one, PAPI3, from a large pond (Fig. 4) outside the western edge of the tailings. The bottom of Lake Parosjärvi is characterized by reductive conditions, but a seasonal water cycle mixes the oxidative surface water with the hypolimnetic water (Parviainen 2012). The Lake Parosjärvi water samples were taken from a water depth of approximately 10 cm, and the other surface water samples were taken from a water depth of approximately 5 cm.

2.2. Haveri, Pirkanmaa, Finland

At the Haveri study area, located 25 km northwest of Ylöjärvi, Pirkanmaa, there was a Au–Cu mine in operation from 1942 to 1960, exploiting different deposits than the former Ylöjärvi mine: The former Haveri Au–Cu mine exploited mainly pyrrhotite-chalcopyrite-

dominated sulfide deposits occurring in mafic tholeiitic metavolcanic rocks (Mäkelä 1980, Eilu 2012). The deposit lies in the western part of the Paleoproterozoic Tampere Schist Belt. A total of about 1.6 Mt of ore was mined, resulting in 1.4 Mt of tailings (Puustinen 2003, Tornivaara et al. 2018). Parviainen (2009) reported the main sulfides in the Haveri tailings to be pyrrhotite and pyrite. The tailings pile is 2–9 m thick with an average thickness of 6.5 m, and covers an area of about 18 ha (Parviainen 2012). The grain size of four tailings samples collected at the Haveri study area was mostly that of silt and fine sand (Parviainen 2009).

Soil in the study area consists mostly of tailings, glaciolacustrine sediments, and sandy till. Mining activities resulted in piling of the tailings in a bay of Lake Kirkkojärvi on top of widely occurring glaciolacustrine silt and clay deposits (Parviainen 2012). East of the tailings pile, the soil consists mostly of sandy till. A dam was built around the former tailings pile (Fig. 5) of natural soil and crushed bedrock. During active mining, the tailings dam failed in the NE near the sampling point HAPI1, resulting in tailings material inundating the lake shoreline.

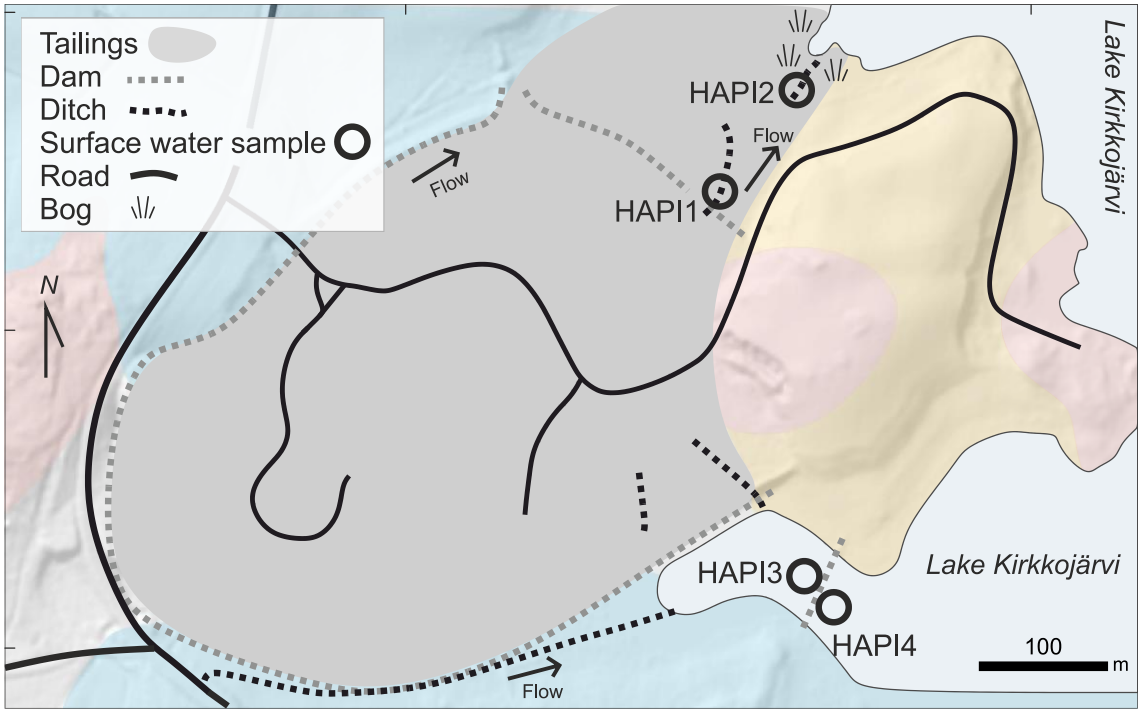

Figure 5. Generalized map of the Haveri study area (modified from Placencia-Gómez et al. 2010). Hillshade data is modified from National Land Survey of Finland (2019). Red color represents exposed bedrock and areas with a thin cover (<1 m) of Quaternary deposits, brown color represents sandy till deposits, and blue color represents clay and silt deposits (modified from National Land Survey of Finland 2019).

Figure 6. Tailings runoff sampling point HAPI1. The photo was taken facing NE towards Lake Kirkkojärvi.

During the later states of mining, tailings was piled directly into Lake Kirkkojärvi outside the dam structure (Parviainen 2012). During field work, it was observed that mechanical reworking of the top layer of the tailings was underway in the central part of the tailings pile, S-SW of the HAPI1 sampling point.

On the NE side of the failed dam, there is runoff-caused erosion on the surface of the tailings material with runoff flowing to the NE (Fig. 6), as the pile slopes toward the lake (Valo 2012). Surface water in the study area drains mainly east to Lake Kirkkojärvi (≈0.7 km^2), which is connected to Viljakkalanselkä and Lake Kyrösjärvi (96 km^2). Major ditches in the area can be seen in Figure 5.

Water samples were collected from two tailings runoff locations, one from the tailings sedimentation basin from a water depth of 0–5 cm, and one from the shore of Lake Kirkkojärvi from a water depth of 0–5 cm. At the tailings area, the groundwater level is about 2 m below surface also flowing mainly to the NE (Valo 2012). There is an aquifer, Haveri (0.52 km^2), located west of the study area. The aquifer is, at closest, about 500 m from the tailings, with an estimated flow rate of 180 $m^3\ d^{-1}$ (Finnish Environment Institute

2019). The aquifer is classified as being in good chemical condition and as not being in risk of contamination (Finnish Environment Institute 2019).

2.3. Pyhäsalmi, North Ostrobothnia, Finland

The Pyhäsalmi study area (Fig. 7) is located 2–5 km SE of the Pyhäjärvi town center in North Ostrobothnia, Finland. The Pyhäsalmi Zn–Cu mine deposit, hosted by rhyolitic and basaltic volcanic rocks (Mäki et al. 2015), has been exploited since 1962 (Haapala and Papunen 2015), and is located in the Vihanti-Pyhäsalmi volcanogenic massive sulfide (VMS) belt.

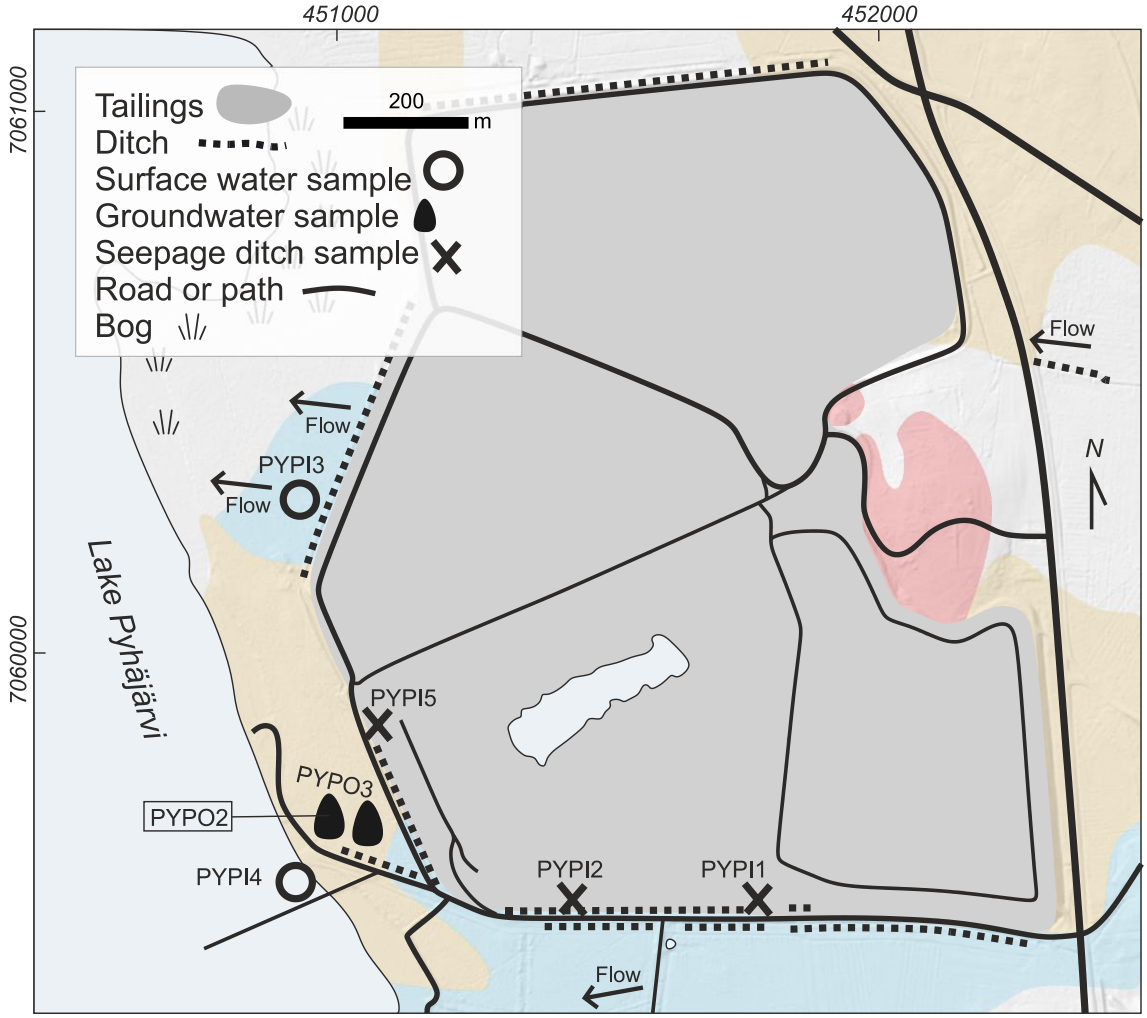

Figure 7. Generalized map of the Pyhäsalmi study area. Surface and seepage water flow directions (modified from Räisänen and Skinnari 2015 and National Land Survey of Finland 2019) are depicted as arrows. Hillshade data is modified from National Land Survey of Finland (2019). Red color represents exposed bedrock and areas with a thin cover of Quaternary deposits, brown color represents fine till deposits, and blue color represents clay and clayey till deposits (modified and generalized from Räisänen and Skinnari 2015 and National Land Survey of Finland 2019).

Pyhäsalmi ore is predominantly pyrite, and partially sphalerite [(Zn,Fe)S], chalcopyrite, and pyrrhotite (Helovuori 1979, Luukkanen et al. 2003). In 2003, Luukkanen et al. (2003) reported the estimated amount of pyrite concentrate produced each year to be 0.75 Mt. Toropainen and Heikkinen (2006) reported >40% of the tailings minerals in Pyhäsalmi mine being sulfide minerals, and 38.4% of the tailings minerals being pyrite.

All three tailings seepage collection ditch samples in this study, of which the sampling point PYPI5 is pictured in Figure 8, were collected at the Pyhäsalmi study area. Water in the Pyhäsalmi seepage collection ditches is eventually pumped back into the tailings system. At the Pyhäsalmi study area, also one surface water sample, PYPI3, was collected from a shallow forest puddle outside the seepage collection ditch along the western edge of the tailings piles, and one surface water sample, PYPI4, from the shore of Lake Pyhäjärvi (122 km^2) from a water depth of approximately 20 cm. Groundwater samples were collected from two monitoring wells, PYPO2 (Fig. 9) and PYPO3, pumped earlier in the month and allowed to settle.

Figure 8. Tailings seepage collection ditch sampling point PYPI5. Photo taken facing S-SE.

Soil in the study area, excluding the tailings, consists predominantly of fine-grained till deposits with thicknesses of 5 to 15 m, and is partially overlain by peat, clay, silt and/or fine sand (Räisänen and Skinnari 2015). The tailings piles, covering an area of about 150 ha, were built on fine-grained till deposits and peat (Nenonen 1995). The piles lie in a bedrock depression, and consist of about 10 Mt of tailings (Toropainen and Heikkinen 2006, Räisänen and Skinnari 2015). In the area between the tailings and Lake Pyhäjärvi the bedrock is at a depth of 2.1 to 4.7 m below ground surface, and, in previous studies, to the north and south of the tailings the bedrock was found to be at >10 m depth in four study locations (Nenonen 1995).

Groundwater and surface water at the tailings piles drains mainly into seepage collection ditches on the S, SW, and NW edges of the tailings (Räisänen and Skinnari 2015). Surface water in all directions outside the tailings piles flows mainly west towards Lake Pyhäjärvi. The nearest classified aquifers in the POVET database (Finnish Environment Institute 2019) are located >15 km from the study area.

Figure 9. Groundwater monitoring well sampling point PYPO2. Photo taken facing east towards the tailings.

3. MATERIALS AND METHODS

The total number of waters sampled was 20, of which 11 were surface waters, three were tailings seepage collection ditches, and six were groundwater wells.

3.1. Sample collection, handling and preservation

In all three study locations, water samples were collected in late May 2019 in the vicinity of mine tailings impoundments at a snow-free time. From all but one sample point, three water samples were collected for different analyses. The water samples consisted of: 1) a raw water sample, 2) a filtered and EDTA-preserved sample, and, 3) a filtered and HNO_3-preserved sample.

19 raw water samples were collected in 500 ml polyethylene bottles for alkalinity and major ion composition analyses. To enhance sampling accuracy, the 500 ml bottles were rinsed three times with sample water before collecting the actual sample. A telescopic rod was used in surface water sampling when necessary. A 500 ml sample was not collected for the bog sampling point PAPI2 because the water was too shallow for sampling. In all study areas, disposable bailers were used for collecting the groundwater well samples from the top 1 m below the groundwater table in all monitoring wells. The Pyhäsalmi study area groundwater samples were collected from wells pumped earlier in the month and allowed to settle.

Ratios of arsenic species in environmental water samples can change noticeably during storage due to reduction and oxidation, adsorption, and microbial activity, depending on, e.g., oxicity, acidity, and Al, Fe, and Mn concentrations in the solution (Bednar et al. 2002, Polya et al. 2003, Agilent Technologies 2009). Changes in arsenic speciation during storage are normally suppressed by filtration, addition of an adequate preservative, storage in the dark in low temperature, and minimization of storage time (Polya et al. 2003, Wolf et al. 2011, Larios et al. 2012, Sorg et al. 2014, Donner et al. 2017). Bednar et al. (2002) found the change during a 3-month period in As(III)/As(V) ratio in filtered EDTA-preserved samples to be –5 and +3%.

The EDTA- and HNO_3-preserved aliquots in this study were obtained by passing raw water through 0.45-µm polypropylene filters into 15 ml polypropylene tubes, each containing either 100 µL of 0.2 M EDTA, or, 50 µL of 14 M HNO_3, until 10 ml of aliquot was collected. EDTA was added to the arsenic speciation analysis filtrates in order to, e.g., chelate metal cations, reduce microbial activity, and buffer the pH of the sample. When filtering the samples, exposure to air was kept at a minimum. Storage time was minimized, and the samples were transferred to the laboratory in an ice box. In the laboratory, the samples were stored in the dark in 2–5 °C until analysis.

3.2. Sample preparation and analyses

All samples were analyzed in the environmental laboratories of the Department of Geosciences and Geography in the University of Helsinki. Elemental and ionic concentrations were compared with previous local studies and nation-wide elemental and ionic concentration data covering stream waters (Lahermo et al. 1996) and well waters (Lahermo et al. 2002).

3.2.1. Field measurements

During the study site visits field measurements were made using a YSI Professional Plus handheld multiparameter meter for pH, water temperature, dissolved oxygen (DO) concentration, oxidation–reduction potential (ORP) and specific electrical conductance (EC). Field measurements could not be made for the sampling point PAPI2 in Ylöjärvi because the water was too shallow for measurement. The Ylöjärvi groundwater sample temperature values should only be seen as approximate values because of observed temperature changes caused by radiation from sunlight and >20 °C air temperature during the field measurements. Temperatures measured in the field were used for ORP to redox potential (Eh) conversion calculations: ORP values were corrected to the standard hydrogen electrode. YSI Professional Plus pH calibration was verified with a two-point calibration each day the instrument was used.

3.2.2. Trace elements and dissolved arsenic

Two to three weeks after sample collection, 22 HNO_3-preserved samples, including two field duplicates, were analyzed for dissolved arsenic concentrations, and also Cd, Co, Cr, Cu, Fe, Mo, Mn, Ni, P, Pb, Se, Si, U, V, and Zn concentrations on an Agilent 7800 ICP-MS according to the ISO 17294-2 standard. Large elemental maximum concentrations expected in the majority of samples required dilution of the HNO_3-preserved samples in the lab. Also, 13–14 weeks after sample collection, 22 EDTA-preserved samples, including two field duplicates, were analyzed for dissolved arsenic on the mass spectrometer.

Of the 22 EDTA-preserved samples, samples PAPI1–5 and PAPO1–4, collected at the Ylöjärvi study area, were all diluted for analysis. ICP-MS is a commonly used analytical technique for analyzing the trace elements of environmental water samples.

3.2.3. Major ions

Raw sample water (Fig. 10) was analyzed 7 to 14 days after sample collection for alkalinity using TitroLine 5000 equipment according to the SFS-EN ISO 9963-1 standard, and for major ion composition (Ca, Cl, F, K, Mg, Na, and SO_4) using a Metrohm MIC-12 ion chromatography (IC) system with a Metrohm 788 sampler (Fig. 11), according to SFS-EN ISO 10304-1 and SFS-EN ISO 14911 standards. All samples except lake water samples, from all study areas, were diluted for IC analysis.

In IC analysis, NO_3 and PO_4 were not analyzed since a guided maximum recommended time from sampling, 48 h (Finnish Standards Association SFS 1990), had passed. Also, 12–13 weeks after sampling, Cl was analyzed separately for the water samples PAPI1, PAPI3, PAPO1–4, and PYPO2, and these results were included to the study. For this separate Cl-analysis, a guided maximum recommended time from sampling, 28 days (SFS 1990), had passed, and therefore these Cl concentration results should be considered as possibly biased.

Figure 10. A selection of raw water samples collected in 500 ml polyethylene bottles.

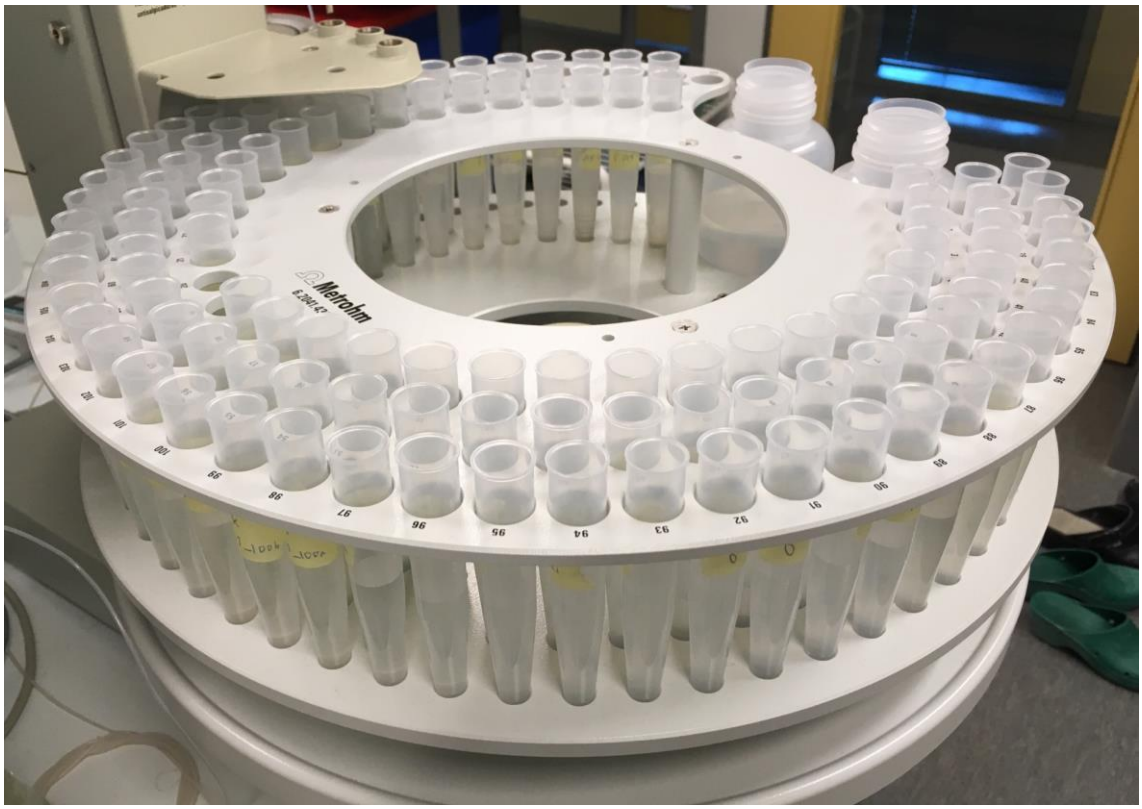

Figure 11. A photograph of water samples being analyzed for major ion composition using a Metrohm MIC-12 ion chromatography (IC) system with a Metrohm 788 sampler.

Alkalinity was determined in the laboratory by titration, carried out to a set pH 4.5 end-point after warming the samples and certified reference materials to 25 ºC in a water bath. Groundwater well samples PAPO1 and PAPO3 were diluted (1+1) for titration with Milli-Q water. Alkalinity values were not determined for the eight samples that had a pH of ≤4.5. These samples were marked as having an alkalinity value of zero. In pH of <4.3, HCO_3 converts into H_2O and CO_2 (Lahermo et al. 1996). Alkalinity values between 4.5 and 8.0 were considered to be 100% HCO_3 and therefore, all alkalinity values were reported as HCO_3 in mmol L^{-1}.

3.2.4. Ionic balance

Ionic balance (IB) percentages were calculated for each sample encompassing Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Mn^{2+}, Fe^{2+}, and Zn^{2+} as cations, and F^-, Cl^-, SO_4^{2-}, and HCO_3^- as anions. Al^{3+}, Mn^{2+}, Fe^{2+}, and Zn^{2+} were included in the IB calculations because of their significant concentrations in some of the water samples.

A zero HCO_3^- value was used in IB calculations for seven samples having a pH(lab) of <4.5. Using the following equation, the number of positively charged ions in each water sample should balance the number of negatively charged ions in each sample:

$$\frac{\Sigma\text{cations} - \Sigma\text{anions}}{\Sigma\text{cations} + \Sigma\text{anions}} \; x \; 100\% \qquad (5)$$

A perfect ionic balance would result in an error value of ±0%. Samples having an error value of <±20% were included to the statistical analyses.

3.2.5. Arsenic speciation

13–14 weeks after sample collection, 1000 µL of each 22 EDTA-preserved aliquots, including two field duplicates, was placed into Agilent 1000 µL PP cartridges for arsenic speciation analysis, using a method described by Day et al. (2002), on an Agilent 1260

liquid chromatograph (LC) coupled to an Agilent 7800 mass spectrometer. Samples PAPI1–5 and PAPO2–4 were diluted in the lab using ultrapure Milli-Q water and EDTA.

Table 2. Operating conditions of the HPLC-ICP-MS system.

HPLC	
Sampler	Agilent 1260 Infinity autosampler
Analysis mode	Isocratic
Column	G3159-65001 (4.6 mm x 150 mm)
Stationary phase	Hydrophilic polymethacrylate as basic resin
Mobile phase	2.0 mM PSB/0.2 mM EDTA (pH 6.0)
Flow rate	1000 µL min^{-1}
Injection volume	100 µL
Sample loop	100 µL

ICP-MS	
RF power	1600 W
Sample depth	8.0 mm
Carrier gas flow rate	1.05 L min^{-1}
Spray chamber temperature	2.0 °C
Nebulizer pump	0.5 rps
Interference control	He
He flow	4.0 mL min^{-1}
Kinetic energy discrimination	2.5 V
Analysis mode	Time resolved analysis
Integration time	1.0 s
Total sampling time	11 min

High performance liquid chromatography–inductively coupled plasma mass spectrometry (HPLC-ICP-MS) is a well-established and precise analytical technique for determining arsenic species in aqueous solutions in research fields such as earth, environmental, and life sciences (Polya et al. 2003, Ma et al. 2014). In this study, dissolved As(III), As(V), monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) were chromatographically separated from the EDTA-preserved samples in 11 minutes. Speciation analyses were performed in time resolved analysis (TRA) mode using an integration time of 1 s, and the detection limits for the arsenic species were calculated experimentally. Agilent MassHunter 4.5 software was used for the arsenic speciation data processing and analysis. The operating conditions for the HPLC-ICP-MS system are shown in Table 2.

The sums of the arsenic species' concentrations were compared with the total dissolved arsenic concentration. In a perfect analysis, if the dissolved arsenic in the water samples

consisted entirely of As(III), As(V), DMA and MMA, the sum of the species' concentrations and the total dissolved arsenic concentration would equal.

3.2.6. Blanks, duplicates and reference materials

Reagent blank matrices, duplicates, and certified reference materials were used in all ICP-MS and IC analyses. Blank matrices' concentrations exceeding the method detection limit (MDL) were reduced from the measured sample concentrations. In ICP-MS analyses, the refererence material used was SPS-SW1, batch 122, and in IC analyses and titration, the reference material used was VKI QC DWB, 'major components in drinking water', batches VKI-16-4-0199 and VKI-16-5-0199. The arsenic standard source used in speciation analyses was a stock standard solution by SPEX CertiPrep Inc. In IC analyses, duplicate and triplicate concentration results were compared using relative standard deviation (RSD), for which values of ≤15% were considered acceptable. For the samples from the Ylöjärvi study area, one duplicate sample and one triplicate sample were analyzed using IC, and one field duplicate was prepared for ICP-MS and HPLC-ICP-MS analyses under identical conditions. For the samples from Haveri, two triplicate samples were analyzed using IC. For the samples from Pyhäsalmi, two triplicate samples were analyzed using IC, and one field duplicate was prepared for ICP-MS and HPLC-ICP-MS analyses.

3.3. Statistical methods and data visualization

Physico- and geochemical information and results were analyzed using Microsoft Excel 2016 and AquaChem 2014.2 for data processing and visualization, and IBM SPSS Statistics 25 for Windows for statistical analysis. CorelDRAW 2018 was used for editing vector graphics. Maps and their measured grid data were created using ESRI ArcMap 10.3.1, and were referenced to the EUREF-FIN-TM35FIN coordinate system.

The Shapiro-Wilk test (Shapiro and Wilk 1965) was applied at the 95% confidence level to test for the statistical normality of the elemental, ionic, and speciation concentrations. For the variables not fulfilling the null hypothesis that the concentration data is normally distributed, a logarithmic transformation was applied. The normally and log-normally

distributed concentration data were compared to each other using bivariate Pearson correlation. Significant correlations at the 0.01 level (2-tailed) were marked with two asterisks (**), and significant correlations at the 0.05 level (2-tailed) were marked with one asterisk (*). A maximum sample size of 22 unique samples in the bivariate correlation analyses of this study can be considered small for geochemical bivariate correlation analysis.

4. RESULTS

4.1. Physicochemical conditions

Table 3. Water type, groundwater well ID, temperature, pH, redox potential (Eh), electrical conductivity (EC), dissolved oxygen (DO) for 20 water samples. Sample IDs beginning with "PA" = Ylöjärvi study area, "HA" = Haveri study area, and "PY" = Pyhäsalmi study area.

Sample	Water type	Well ID	Temp. °C	pH (field)	Eh mV	EC µS cm^{-1}	DO mg L^{-1}
PAPI1	SW		17.2	3.59	351	1655	1.31
PAPI2	SW, bog		na	na	na	na	na
PAPI3	SW, pond		15.8	4.23	314	872	2.68
PAPI4	SW, lake		19.0	5.25	266	88	8.49
PAPI5	SW, lake		19.4	5.18	270	89	8.50
PAPO1	GW	Hp4	7.2	6.36	183	775	1.32
PAPO2	GW	Hp2	6.9	6.31	186	1194	1.17
PAPO3	GW	Hp5	8.5	7.42	132	926	5.36
PAPO4	GW	Hp1	8.0	6.94	159	1311	1.43
HAPI1	SW, runoff		17.0	2.60	405	4749	1.99
HAPI2	SW, bog		18.0	4.41	212	1808	2.41
HAPI3	SW		19.8	5.80	235	299	9.67
HAPI4	SW, lake		22.1	6.20	213	103	8.91
PYPI1	SW, seepage		12.3	4.54	293	1231	8.39
PYPI2	SW, seepage		13.6	3.01	378	2745	7.97
PYPI3	SW, bog		17.1	6.61	195	1488	9.14
PYPI4	SW, lake		11.9	6.25	207	52	11.09
PYPI5	SW, seepage		13.9	2.71	393	5919	3.91
PYPO2	GW	E	5.5	6.32	196	317	1.41
PYPO3	GW	B	5.6	5.24	249	1143	4.49

SW = surface water
GW = groundwater
na = not analyzed

Field measurement results and water type characterization of the 19 water samples and sample locations are presented in Table 3. Surface water samples collected from the Ylöjärvi study area were acidic, with pH values ranging from 3.6 to 5.3. Samples from the four groundwater monitoring wells in the Ylöjärvi study area were more neutral, with pH values ranging from 6.3 to 7.4, with 7.4 being the maximum pH value measured in this study. In the Haveri surface water samples, located in the northeastern part of the tailings pile, pH values ranged from 2.6 to 6.2, with 2.6 being the minimum pH value measured in this study. In the Pyhäsalmi tailings seepage collection ditch samples, pH values varied from 2.7 to 4.5, while all other Pyhäsalmi water samples, located further away from tailings, were notably less acidic, with pH values ranging between 5.2 and 6.6.

Redox potential was positive to highly positive, varying between 132 and 405 mV. Redox potential in the groundwater samples collected at the Ylöjärvi study area varied between 132 and 183 mV, and rose to a range of 266 to 351 mV in the surface water samples located further outside the large tailings pile. The Ylöjärvi groundwater samples had DO concentrations ranging from 1.2 to 5.4 mg L^{-1}, with an arithmetic mean of 2.3 mg L^{-1}, whereas the Ylöjärvi surface water samples had DO concentrations of 1.3 to 8.5 mg L^{-1}, with an arithmetic mean of 5.25 mg L^{-1}. The groundwater well from which the sample PAPO1 was taken, in the southern part of the large Ylöjärvi mine tailings pile, had a characteristic smell of H_2S.

Samples from the two groundwater monitoring wells SW of the tailings in Pyhäsalmi had somewhat similar Eh and DO values as the Ylöjärvi groundwater samples: Eh values in the Pyhäsalmi groundwater samples ranged between 196 and 249 mV, and DO values ranged between 1.4 and 4.5 mg L^{-1}, respectively. In the Pyhäsalmi samples, excluding the groundwater samples, DO values ranged between 3.9 and 11.1 mg L^{-1}, with a relatively high arithmetic mean of 8.1 mg L^{-1}.

EC values had a minimum and maximum of 52 and 5919 μS cm^{-1}. The lowest EC values, 52, 88, 89, and 103 μS cm^{-1}, were measured in Lake Pyhäjärvi, Lake Parosjärvi, Lake Parosjärvi, and Lake Kirkkojärvi, respectively, and the highest EC values, 2745, 4749, and 5919 μS cm^{-1}, were measured in a Pyhäsalmi tailings seepage collection ditch, Haveri tailings runoff, and another Pyhäsalmi tailings seepage collection ditch, respectively. None of the water samples indicated anoxic conditions: DO concentrations exceeded 1.0

mg L^{-1} in all 19 sampling locations, with high values of ≥8.5 mg L^{-1} measured in all sampled lake waters, the Haveri tailings sedimentation basin located on the SE edge of the tailings, and a forest puddle located some tens of meters west of the Pyhäsalmi tailings.

4.2. Elemental concentrations

Concentrations of dissolved elements in 20 water samples collected at the Ylöjärvi, Haveri, and Pyhäsalmi study sites are presented in Table 4a–b. The ionic balances of 19 water samples are presented in Table 5.

Table 4a. Concentrations of dissolved elements in 20 water samples collected at three study areas in Finland. Sample IDs beginning with "PA" = Ylöjärvi study area, "HA" = Haveri study area, and "PY" = Pyhäsalmi study area.

Sample	Al	Cd	Co	Cr	Cu	Mo	Ni	P	Pb	Se	Si	V	U
	mg L^{-1}	µg L^{-1}											
PAPI1	20.8	8.1	2720	0.2	947	0.0	563	9.1	1.1	11.6	9.7	0.1	9.4
PAPI2	0.0	0.0	11.0	0.1	0.4	0.8	2.8	11.7	0.0	0.1	5.9	0.0	0.1
PAPI3	4.5	1.7	508	0.0	711	0.1	83.8	6.7	0.3	1.8	4.4	0.0	6.9
PAPI4	0.3	0.1	11.9	0.2	37.7	0.4	2.9	13.0	0.2	0.1	2.8	0.3	0.2
PAPI5	0.3	0.1	11.8	0.2	36.3	0.4	2.8	8.5	0.1	0.1	3.0	0.3	0.2
PAPO1	0.0	0.0	3.6	0.4	0.3	0.2	3.0	14.7	0.0	0.1	20.5	0.1	0.1
PAPO2	0.1	0.0	106	0.0	0.6	0.7	5.0	8.3	0.0	0.0	3.6	0.0	0.0
PAPO3	0.0	0.0	5.6	0.5	0.1	10.0	6.8	5.0	0.0	0.2	4.0	2.0	1.7
PAPO4	0.0	0.0	36.6	0.3	0.1	3.3	0.7	10.1	0.0	0.1	4.0	0.8	7.8
HAPI1	18.6	2.4	555	8.7	802	0.1	646	56.9	0.6	3.6	40.7	10.4	20.5
HAPI2	1.2	1.2	196	0.6	98.3	0.0	186	48.3	0.1	1.0	25.5	0.6	1.0
HAPI3	0.0	0.0	1.7	0.4	11.1	0.1	6.6	13.5	0.1	0.1	0.9	0.1	0.1
HAPI4	0.0	0.0	0.6	0.1	7.1	0.1	2.7	13.9	0.0	0.1	1.1	0.2	0.1
PYPI1	8.6	2.2	25.8	3.6	500	0.2	22.8	15.7	6.5	0.4	15.8	0.6	1.8
PYPI2	35.9	18.3	102	16.9	1525	0.0	108	28.6	2.2	1.3	25.3	1.1	10.2
PYPI3	0.0	0.1	7.4	0.3	4.1	0.1	5.9	31.8	0.0	0.1	7.9	0.2	0.1
PYPI4	0.1	0.3	0.2	0.2	7.3	0.1	0.6	9.0	0.1	0.1	1.0	0.2	0.1
PYPI5	152	39.7	4744	48.6	2189	0.1	318	97.3	1.1	5.6	51.0	8.1	49.2
PYPO2	0.0	0.0	0.4	0.1	0.7	0.2	0.7	6.1	0.0	0.0	14.3	0.0	0.1
PYPO3	2.9	4.2	28.6	0.6	65.0	0.0	45.9	12.0	0.0	0.2	15.7	0.0	0.3

na = not analyzed

Table 4b. Concentrations of dissolved elements in 20 water samples collected at three study areas in Finland. Sample IDs beginning with "PA" = Ylöjärvi study area, "HA" = Haveri study area, and "PY" = Pyhäsalmi study area.

Sample	Ca	F	Fe	K	Mg	Mn	Na	Zn	Cl	SO_4	HCO_3
	mg L^{-1}										mmol L^{-1}
PAPI1	194	12.8	99.3	22.5	41.5	4.9	11.7	3.2	2.4	962	na
PAPI2	na	na	10.2	na	na	1.9	na	0.0	na	na	na
PAPI3	125	2.0	1.7	20.1	17.9	1.7	11.0	0.3	2.0	449	na
PAPI4	9.1	0.3	0.4	2.1	2.0	0.1	2.6	0.0	2.0	30.8	<0.2
PAPI5	9.1	0.3	0.4	2.0	1.9	0.1	2.5	0.0	1.9	29.7	<0.2
PAPO1	45.7	0.5	12.0	23.2	16.4	0.5	79.2	0.0	6.5	46.7	7.08
PAPO2	160	2.3	2.6	35.5	24.5	3.2	26.1	0.0	2.3	507	0.98
PAPO3	132	2.6	47.0	52.9	9.0	1.6	46.7	0.0	1.9	235	7.84
PAPO4	233	1.3	88.8	42.9	30.4	4.0	10.9	0.0	1.9	680	1.33
HAPI1	442	3.5	614	7.5	272	6.6	28.0	0.7	24.2	4725	na
HAPI2	92.7	0.2	284	11.3	52.1	1.3	17.3	0.2	29.2	978	na
HAPI3	17.8	0.2	0.2	3.4	7.5	0.1	5.2	0.0	4.3	70.4	0.27
HAPI4	8.1	0.1	0.1	2.3	3.6	0.0	3.2	0.0	3.5	21.0	0.34
PYPI1	163	0.7	30.4	6.6	170	1.7	19.6	1.5	29.9	1240	na
PYPI2	266	2.2	71.8	6.2	195	7.1	44.3	7.7	30.4	2231	na
PYPI3	148	0.2	0.5	8.8	116	12.3	27.9	0.0	26.3	917	0.83
PYPI4	4.7	<0.1	0.1	1.1	1.8	0.1	1.9	0.1	2.4	10.4	<0.2
PYPI5	370	7.2	581	<0.3	685	18.5	45.4	23.6	30.9	7109	na
PYPO2	17.9	0.7	4.1	<0.3	19.3	0.7	10.0	0.0	2.6	129	0.79
PYPO3	124	RSD	0.6	<0.3	101	2.0	27.5	0.8	23.3	778	<0.2

Concentrations below the method detection limit are marked with a less-than sign.
RSD = relative standard deviation exceeded 15%, and therefore the result was not included to the study
na = not analyzed

Table 5. Sums of cations and anions in meq L^{-1} and the ionic balance error percentage.

Sample	ΣCat	ΣAn	IB
	meq L^{-1}	meq L^{-1}	%
PAPI1	20.57	20.78	-0.5
PAPI2	na	na	na
PAPI3	9.51	9.51	0.0
PAPI4	0.84	0.78	3.2
PAPI5	0.83	0.77	3.6
PAPO1	8.12	8.27	-0.9
PAPO2	12.29	11.71	2.4
PAPO3	12.45	12.93	-1.9
PAPO4	19.01	15.61	9.8
HAPI1	72.69	99.24	-15.4
HAPI2	20.35	21.19	-2.0
HAPI3	1.84	1.87	-0.8
HAPI4	0.90	0.89	0.9
PYPI1	25.32	26.71	-2.7
PYPI2	39.38	47.42	-9.3
PYPI3	18.87	20.67	-4.6
PYPI4	0.52	0.48	3.5
PYPI5	117.8	149.3	-11.8
PYPO2	3.09	3.58	-7.3
PYPO3	16.15	16.93	-2.3

na = not analyzed

The relative median abundances of the analyzed elements and ions, excluding HCO_3, ranked in the order of SO_4 > Ca > Mg > Na > Fe > K > Cl > Mn > F > Al > Zn > Cu > Co > P > 10 µg L^{-1}, the concentrations of which varied as follows: SO_4 10.5–7109 mg L^{-1}, Ca 4.7–442 mg L^{-1}, Mg 1.8–685 mg L^{-1}, Na 1.9–79 mg L^{-1}, Fe 0.1–614 mg L^{-1}, K 0.0–52.9 mg L^{-1}, Cl 1.9–30.9 mg L^{-1}, Mn 0.0–18.5 mg L^{-1}, F 0.1–12.8 mg L^{-1}, Al 0.0–152 mg L^{-1}, Zn 0.0–23.6 mg L^{-1}, Cu 0.1–2189 µg L^{-1}, Co 0.2–4744 µg L^{-1}, and P 5.0–97.3 µg L^{-1}. No elemental concentrations in the samples analyzed using ICP-MS were less than the MDL.

The ionic balance was between -5 and +5% for 14 of the 19 samples (Table 5). The five samples having an IB error of >5% (PAPO4, HAPI1, PYPI2, PYPI5, and PYPO2) should be considered as possibly biased. In establishing the cation charge, it was assumed that Fe was in the reduced +II state. If Fe would have been assumed to be 100% Fe(III), the average ionic balance error would have changed from -1.9 to -0.1%. The average Fe(II)/Fe(III) ratio of the collected water samples was not analyzed in this study. For the two samples having an error of ≥10.0%, the errors were between -11.8 and -15.4%. The cation sum was lower than that of the anion sum in 13 of the 19 samples, and was composed on average of 13% dissolved Al, Mn, Fe, and Zn, analyzed by ICP-MS, with a maximum of 51% in the HAPI2 bog water sample, colleted at the shore of Lake Kirkkojärvi in the Haveri study area. The anion sums of the five samples having an IB error of >5% were composed of 75 to 99% SO_4 , with an average of 92%. For the majority of the samples, the measured SO_4 concentration was the largest single component affecting the ionic balance.

In 3 cases out of 31, the relative standard deviation (RSD) percentage for the triplicate samples analyzed by IC (Appendix 2) exceeded 10%. The concentration of F for the sample PYPO3, collected from a groundwater monitoring well located some 100 m SW of the Pyhäsalmi tailings, was not included to the study because its RSD exceeded 15%.

IC blank results associated with the water samples were below the method detection limit for Na, K, Ca, Mg, F, and Cl. Blanks analyzed by IC had larger SO_4 concentrations than the SO_4 MDL of 0.07 mg L^{-1} by an average of 0.03 mg L^{-1}, the maximum blank matrix having 0.16 mg L^{-1} SO_4. All associated sample results of SO_4 were more than 50 times

larger than the maximum blank concentration, with a median of >3000 times the maximum blank concentration. The average SO_4 concentration of the blanks that exceeded the method detection limit was reduced from all measured SO_4 sample concentrations.

Figure 12 shows the results of plotting the 19 water samples on the Piper diagram. In the cation triangle, data is broadly distributed in the Ca-Mg side of the triangle, with the Pyhäsalmi tailings seepage collection ditch samples PYPI5 and PYPI1 being the most Mg-dominated samples. In the anion triangle, the majority of the samples were sulphate type, with a distinct cluster of mining-impacted waters forming in the SO_4-tip of the triangle.

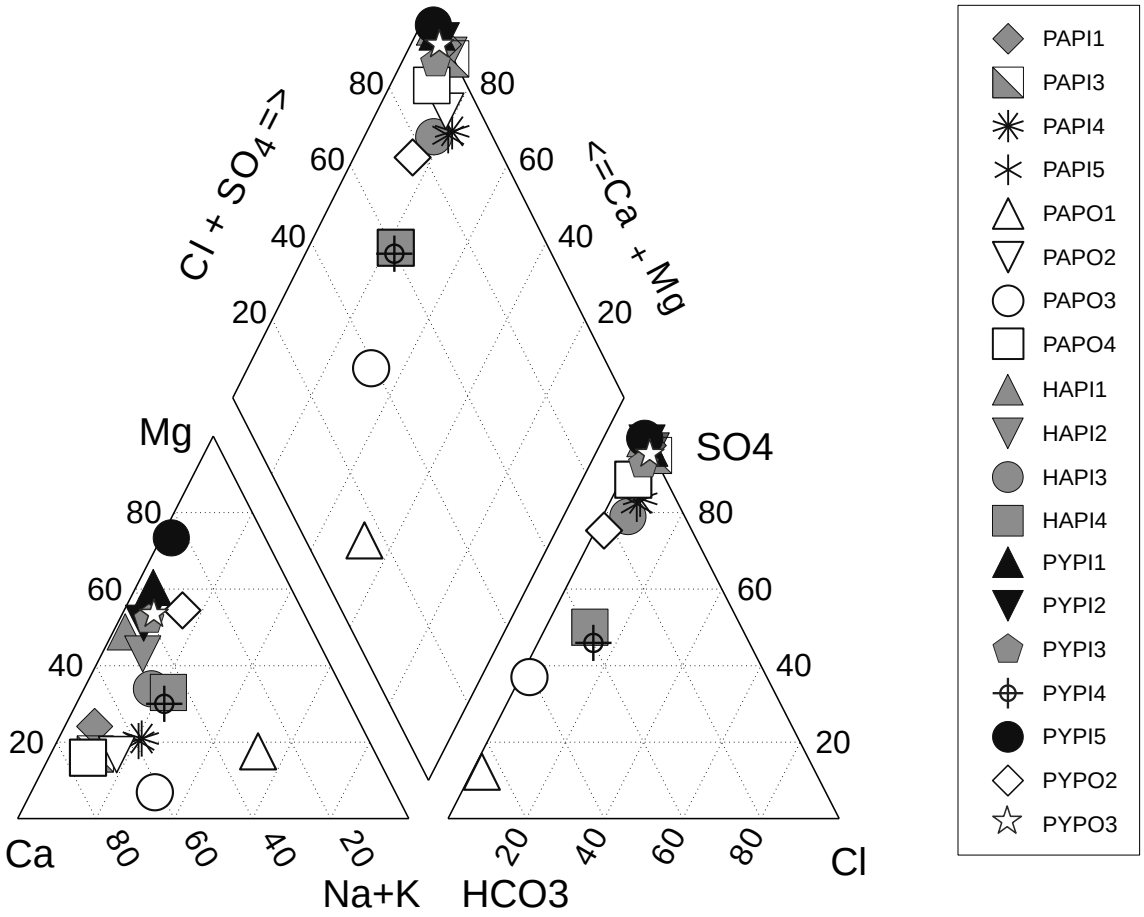

Figure 12. Piper plot showing the chemical compositions of the groundwater samples (white symbols with black outlines), tailings seepage collection ditch samples (black symbols with black outlines), and surface water samples.

A cluster of samples was also formed in the Cl+SO_4-Ca+Mg-tip of the diamond, indicating that for the majority of the samples, strong acids exceed weak acids. Two Ylöjärvi groundwater monitoring well samples, PAPO1 and PAPO3, located in the western and southern parts of the large Ylöjärvi tailings pile, were outliers in the diamond mainly because of their large alkalinity values compared to the other samples.

4.3. Arsenic concentrations and speciation

Concentrations of arsenic and its species in the filtered surface water samples, groundwater samples, and tailings seepage collection ditch samples are shown in Table 6, and Figures 13–16.

Table 6. Dissolved HNO_3-preserved, EDTA-preserved, and average arsenic concentrations, and arsenic speciation results for 22 water samples. PAPI3a–b and PYPI3a–b are field duplicates. Percentages of each arsenic species are percentages compared to the sum of the species' concentrations.

Sample	As (HNO_3) µg L^{-1}	As (EDTA) µg L^{-1}	As (avg) µg L^{-1}	As(III) µg L^{-1}	As(III) %	As(V) µg L^{-1}	As(V) %	MMA µg L^{-1}	DMA µg L^{-1}	Σ(As spec) % of As*
PAPI1	45.6	39.6	42.6	<MDL	–	13.4	–	<MDL	<MDL	31.4
PAPI2	502	247	374	137	–	<MDL	–	<MDL	<MDL	36.7
PAPI3a	21.8	33.5	27.6	12.7	49.1	13.1	50.9	<MDL	<MDL	94.7
PAPI3b	20.4	33.1	26.7	11.8	–	<MDL	–	<MDL	<MDL	43.4
PAPI4	110	106	108	<MDL	–	39.6	–	<MDL	<MDL	36.8
PAPI5	104	106	105	<MDL	–	35.7	–	<MDL	<MDL	34.1
PAPO1	14.2	15.0	14.6	2.5	40.1	3.7	59.9	<MDL	<MDL	42.8
PAPO2	303	296	300	148	–	<MDL	–	na	na	49.5
PAPO3	6649	6518	6583	2169	68.7	988	31.3	<MDL	na	48.0
PAPO4	4218	5941	5079	1067	61.6	666	38.4	<MDL	na	34.1
HAPI1	6.2	4.5	5.3	<MDL	–	na	–	na	<MDL	–
HAPI2	1.6	1.6	1.6	<MDL	–	<MDL	–	<MDL	<MDL	–
HAPI3	0.6	0.6	0.6	<MDL	–	<MDL	–	<MDL	<MDL	–
HAPI4	0.5	0.5	0.5	<MDL	–	<MDL	–	na	na	–
PYPI1	1.4	1.3	1.3	<MDL	–	<MDL	–	<MDL	na	–
PYPI2	2.8	2.7	2.7	<MDL	–	<MDL	–	<MDL	<MDL	–
PYPI3a	1.3	1.2	1.3	<MDL	–	<MDL	–	<MDL	<MDL	–
PYPI3b	1.3	1.2	1.3	<MDL	–	na	–	na	<MDL	–
PYPI4	0.5	0.4	0.5	na	–	<MDL	–	<MDL	na	–
PYPI5	9.4	7.7	8.6	<MDL	–	<MDL	–	<MDL	<MDL	–
PYPO2	0.3	0.2	0.3	na	–	<MDL	–	<MDL	<MDL	–
PYPO3	0.4	0.3	0.4	<MDL	–	<MDL	–	<MDL	na	–

* = Measured arsenic speciation sum as a percentage of the total dissolved arsenic concentration
<MDL = concentrations were below the method detection limit
na = not available

4.3.1. Arsenic concentrations

In the HNO_3-preserved water samples, dissolved arsenic concentrations ranged from a low of 0.3±0.02 to a high of 6649±332 µg L^{-1} (n=20; Table 6, Fig. 13), and varied regionally. In the EDTA-preserved water samples, dissolved arsenic concentrations ranged from a low of 0.2±0.01 to a high of 6518±61 µg L^{-1} (n=20). When using an average of the HNO_3-preserved concentration and the EDTA-preserved concentration for each sample, dissolved arsenic concentrations ranged between 14.6 and 6583 µg L^{-1} in the Ylöjärvi study areas water samples, between 0.5 and 5.3 µg L^{-1} in the Haveri study area samples, and between 0.3 and 8.6 µg L^{-1} in the Pyhäsalmi study area samples. Dissolved arsenic concentrations in the HNO_3-preserved samples had an arithmetic mean of 600 µg L^{-1} and a median of 7.8 µg L^{-1}, compared with 666 and 6.1 µg L^{-1} in the EDTA-preserved samples, respectively. After running the Shapiro-Wilk test and performing logarithmic transformations (Appendix 3), the dissolved arsenic concentrations of the HNO_3-preserved and the EDTA-preserved samples showed a highly significant 2-tailed Pearson correlation with each other (r=0.997**, n=20; Appendix 4).

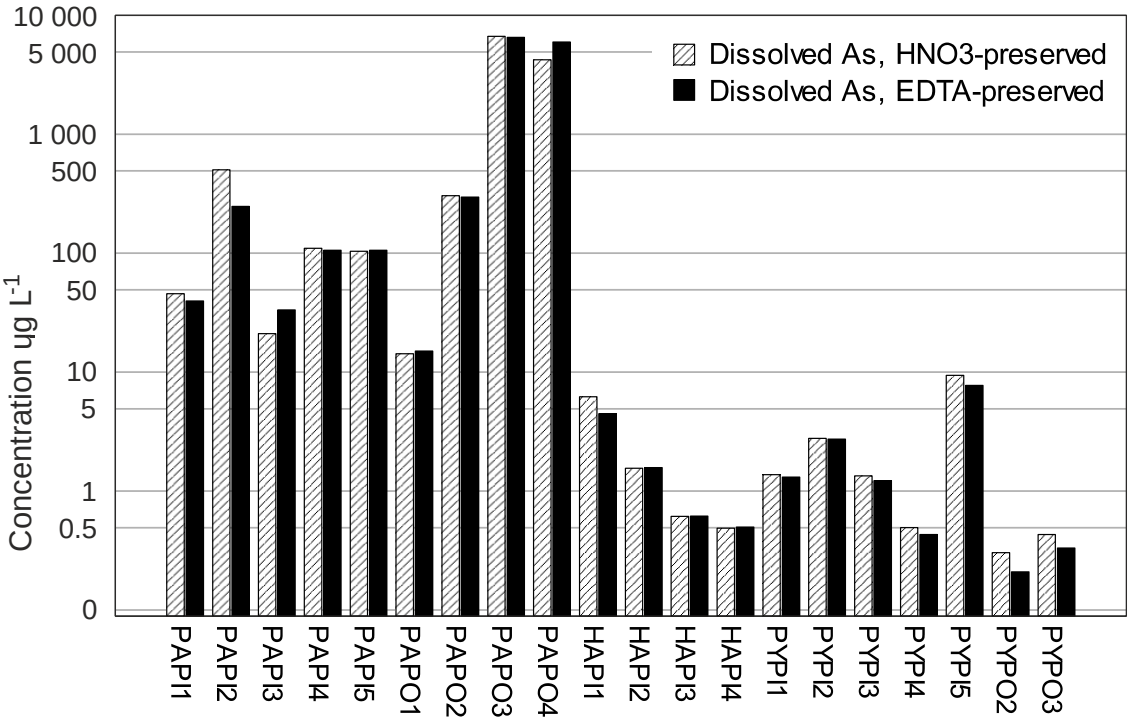

Figure 13. Column chart showing the difference in the dissolved arsenic concentrations between HNO_3-preserved and EDTA-preserved water samples. Study sites are listed from left to right in order from the Ylöjärvi study area to the Haveri and Pyhäsalmi study areas. For locations of sample ID's see Figures 2, 5, and 8.

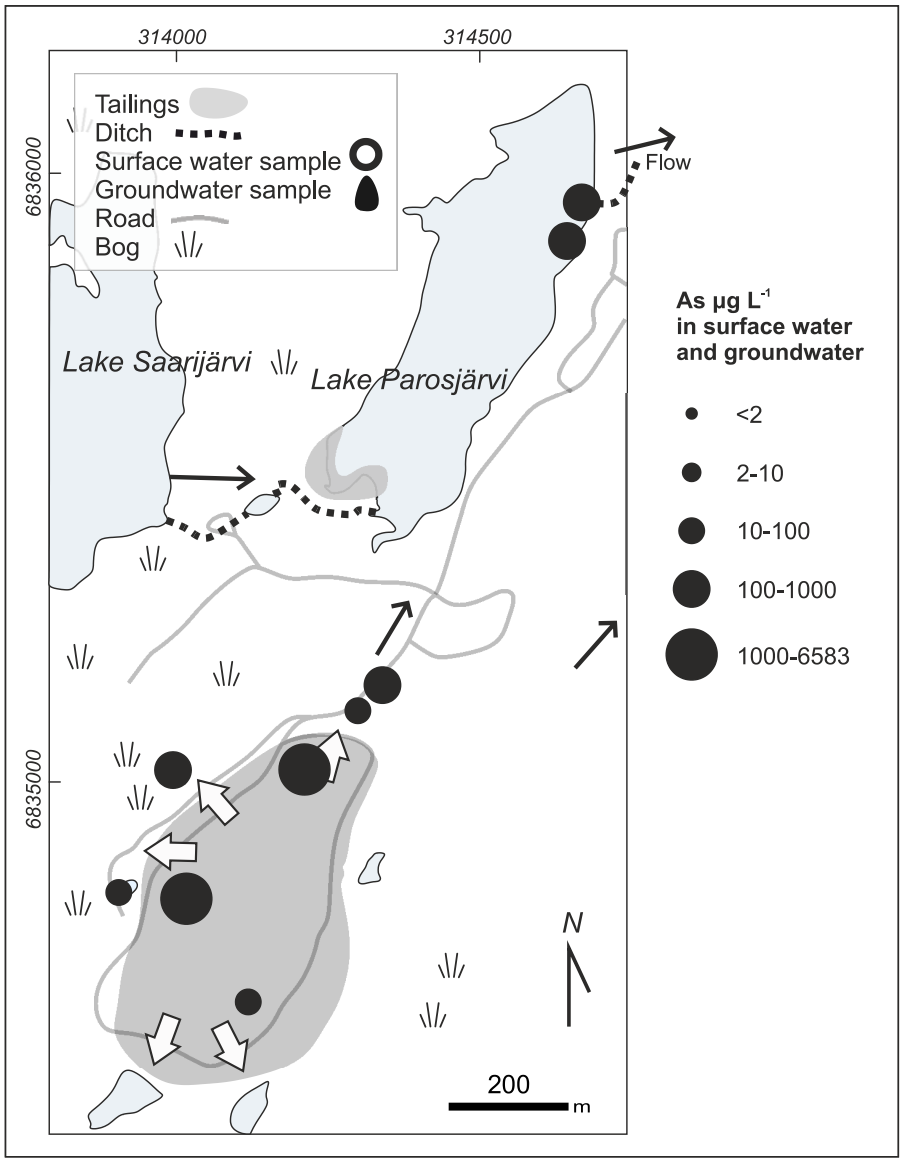

Figure 14. Dissolved arsenic concentrations in groundwater wells and surface waters in the Ylöjärvi study area in 2019. The areal extents of the tailings deposits were modified from Carlson et al. (2002) and Parviainen et al. (2012), and the surface flow directions, depicted as arrows, were modified from Parviainen et al. (2012) and National Land Survey of Finland (2019). Groundwater flow directions (modified from Carlson et al. 2002) are depicted as white arrows.

Dissolved arsenic was found to be abundant in all water samples collected at the Ylöjärvi study area, especially in the groundwater wells PAPO3 and PAPO4 located at the western and nothern edge of the large Ylöjärvi mine tailings pile (Fig. 14). Dissolved arsenic concentrations in groundwater wells PAPO3 and PAPO4 averaged 6583 and 5079 µg L^{-1} arsenic, respectively. All Ylöjärvi study area water samples had >10 µg L^{-1} dissolved arsenic, while all other water samples had <10 µg L^{-1} dissolved arsenic. The median dissolved arsenic concentration in the Ylöjärvi water samples, 108 µg L^{-1}, equalled about 90 times the median value of the Pyhäsalmi and Haveri water samples, a

difference that can also be seen by comparing Figures 14–16. Since only a few samples had particularly high dissolved arsenic concentrations, the median concentration of dissolved arsenic for the 20 unique samples, 6.9 µg L^{-1}, was about 90-fold smaller than the arithmetic mean of the samples, 633 µg L^{-1}.

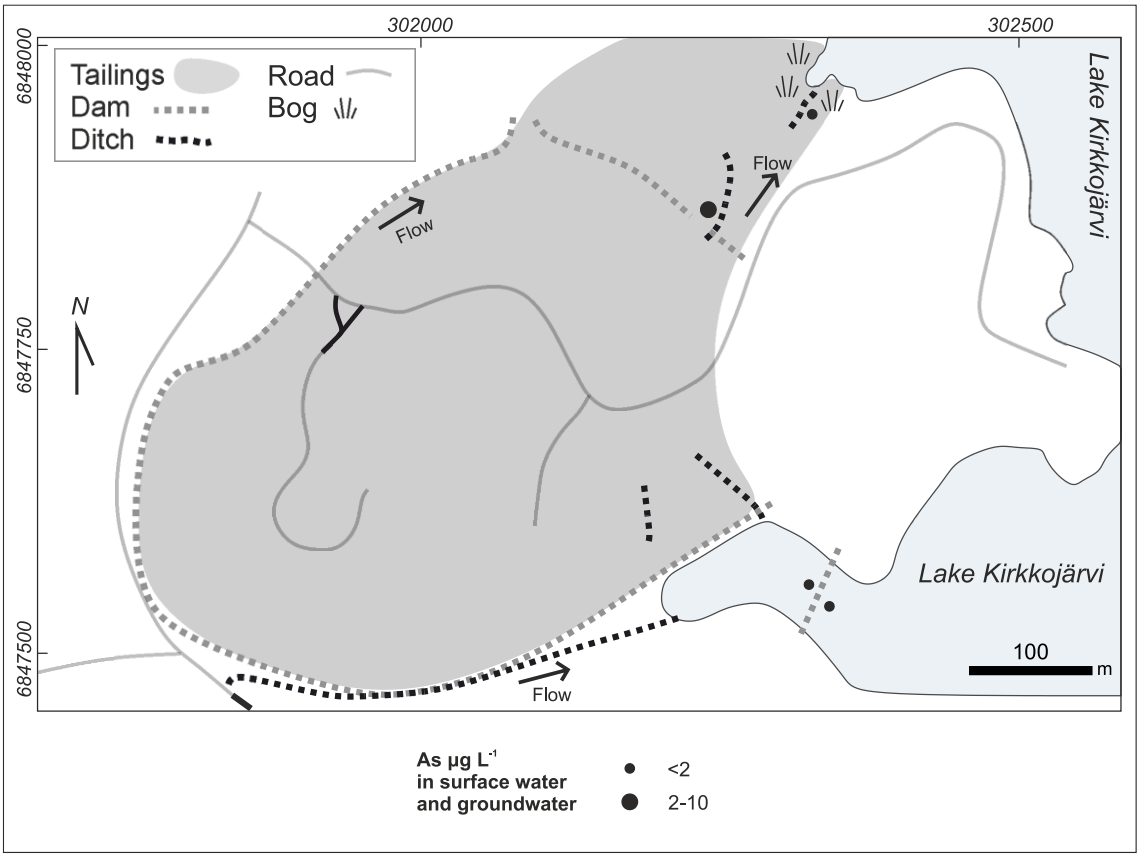

Figure 15. Dissolved arsenic concentrations in surface water in the Haveri study area in 2019. The generalization of the map was modified from Placencia-Gómez et al. (2010).

In the Haveri study area, dissolved arsenic concentrations in the two tailings runoff samples averaged 1.6 and 5.3 µg L^{-1}, whereas in the tailings sedimentation basin water sample and the lake water sample the dissolved arsenic concentrations had reduced to averages of 0.6 and 0.5 µg L^{-1} (Fig. 15). In the Pyhäsalmi study area samples, on average, dissolved arsenic concentrations in the seepage collection ditch samples consisted of 1.3 to 8.6 µg L^{-1} arsenic, indicating dissolution of arsenic from the tailings, whereas the lake, bog, and groundwater samples had low dissolved arsenic concentrations of 0.3 to 1.3 µg L^{-1} (Fig. 16).

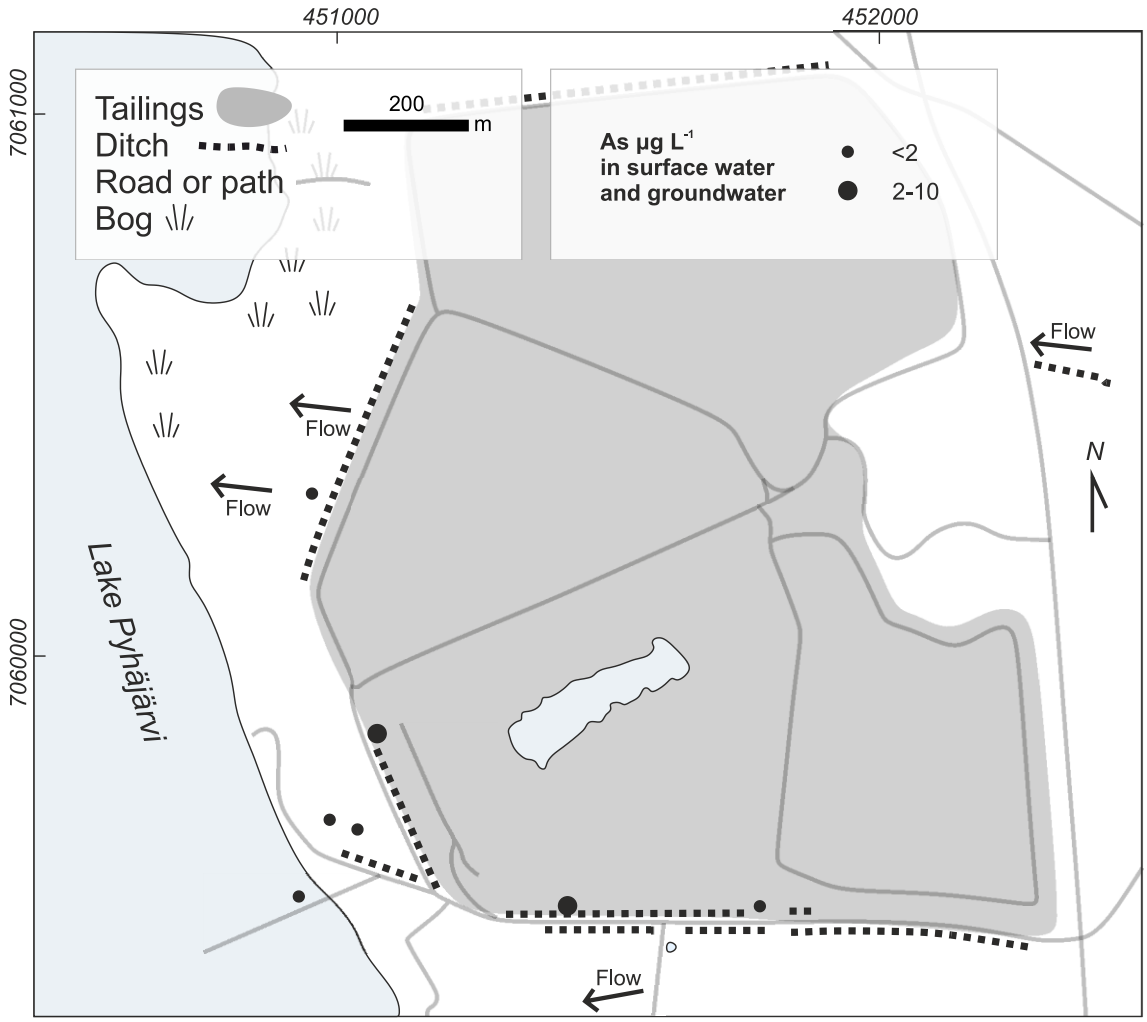

Figure 16. Dissolved arsenic concentrations in tailings seepage collection ditches, groundwater, and surface water in the Pyhäsalmi study area in 2019. The surface and seepage water flow directions (modified from Räisänen and Skinnari 2015 and National Land Survey of Finland 2019) are depicted as arrows.

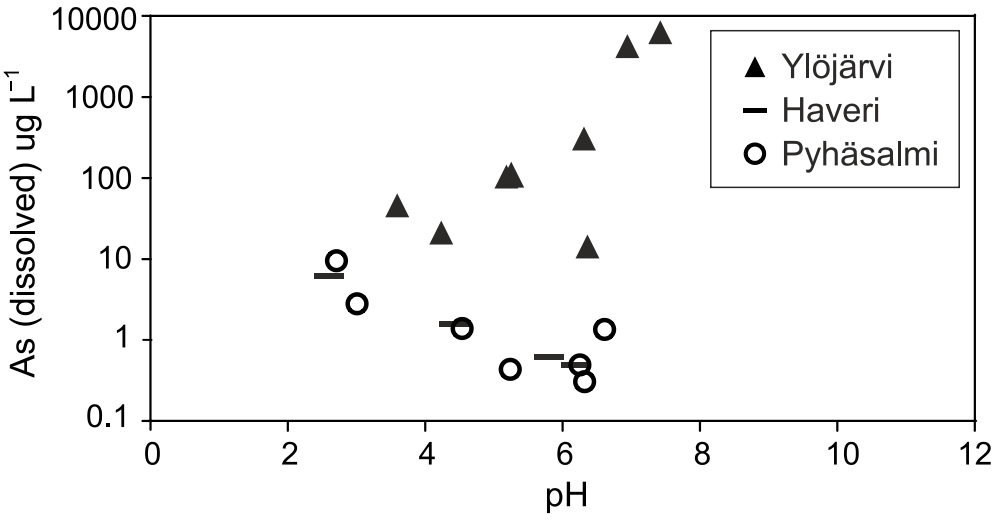

Figure 17. Dissolved arsenic as a function of pH of the 19 water samples by study areas.

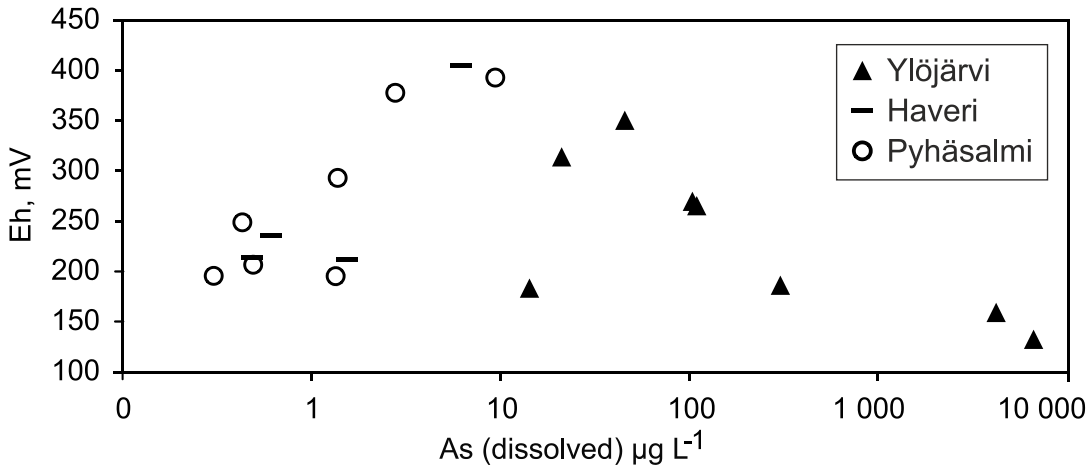

Figure 18. Redox potential as a function of dissolved arsenic of the 19 water samples by study areas.

Dissolved arsenic showed a statistically insignificant correlation with pH (r=0.23, n=19; Fig. 17), Eh (r=-0.22, n=19; Fig. 18), EC (r=0.12, n=19), and DO (-0.34, n=19). In Figures 17 and 18, the water samples collected at the Ylöjärvi study area appear as a separate group having >10 µg L^{-1} arsenic in all samples, while the samples collected at the Haveri and Pyhäsalmi study areas overlap, appearing together as the other group having <10 µg L^{-1} arsenic in all samples. It must be noted that when the correlation analysis was run excluding the Ylöjärvi water samples, dissolved arsenic showed a significant positive correlation with the EC (r=0.81**, n=11) and Eh (r=0.84**, n=11), and a significant negative correlation with pH (r=-0.87**, n=11), indicating a possible different relationship of arsenic to the EC, pH, and Eh in the samples collected at the Pyhäsalmi and Haveri study sites compared with the relationship of arsenic to these parameters in all samples. These relationships can also be seen in Figures 17 and 18, where the sample PAPO1, collected from a groundwater well in the southern part of the large tailings pile at the Ylöjärvi study area, is a sole outlier.

Dissolved arsenic showed a significant 2-tailed Pearson correlation with Mo (r=0.80**, n=20; Fig. 19, Appendix 4) and K (r=0.68**, n=19). In Figure 19, sample PAPI1 is an outlier with 0.04 µg L^{-1} dissolved Mo and 42.6 µg L^{-1} dissolved arsenic. In all samples, dissolved arsenic showed a negative correlation with Cl (r=-0.51*, n=19), while the Pearson correlation of dissolved Mo with dissolved K was 0.497* (n=19). Also, in all samples, dissolved arsenic showed an insignificant correlation with dissolved Fe (r=0.30; Fig. 20), however, when the correlation analysis was again run excluding the Ylöjärvi

water samples, dissolved arsenic showed a significant positive correlation with dissolved Fe (0.81**, n=11).

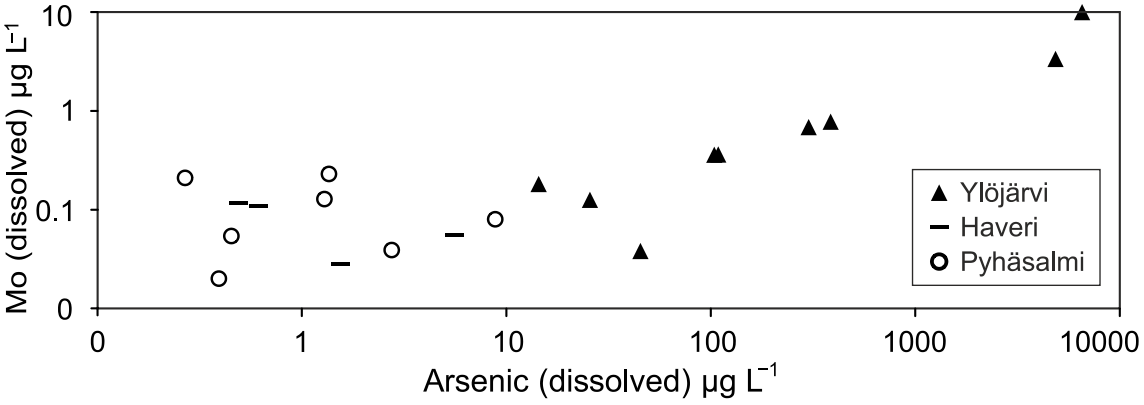

Figure 19. Dissolved Mo as a function of dissolved arsenic.

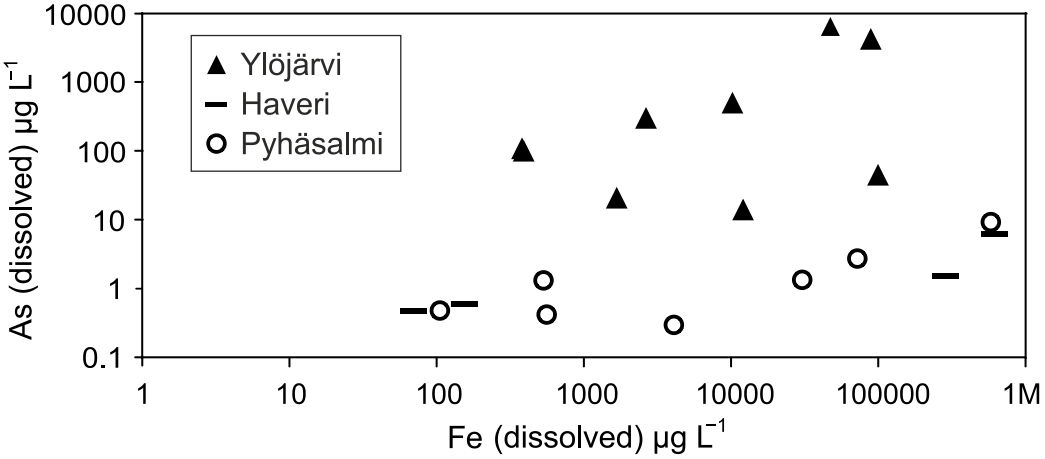

Figure 20. Dissolved arsenic as a function of dissolved Fe.

The water samples collected at the Ylöjärvi study area had a higher dissolved arsenic/Fe ratio than the water samples collected at the Haveri and Pyhäsalmi study areas. The dissolved arsenic/Fe ratio of the Ylöjärvi study area water samples, ranging between 0.000 and 0.284, was on average about 40 times larger than that of the Haveri samples, ranging between 0.000 and 0.007, and on average about 90 times larger than the ratio of the Pyhäsalmi samples, ranging between 0.000 and 0.004. The largest dissolved arsenic/Fe ratios in this study, 0.284 and 0.269, were measured in the Lake Parosjärvi samples PAPI4 and PAPI5.

4.3.2. Arsenic speciation

Concentrations of dissolved As(III) ranged from a low of non-detected to a high of 2169 µg L^{-1}, and concentrations of dissolved As(V) ranged from a low of non-detected to a high of 988 µg L^{-1} (n=22; Table 6, Fig. 22). Speciation data showed that for six samples either dissolved As(III) or As(V) was the dominant iAs specie (>70%): in three samples As(III) was the dominant specie, and in three samples As(V) was the dominant specie. In four samples, the fraction of both As(III) and As(V) ranged between 30% and 70%. The total dissolved arsenic concentrations and the sums of the dissolved arsenic species' concentrations showed a highly significant 2-tailed Pearson correlation with each other (r=0.993**, n=9; Fig. 23).

Both dissolved As(III) and As(V) concentrations varied regionally: in the samples collected at the Ylöjärvi study area, concentrations of As(III) and As(V) ranged between <MDL and 2169 µg L^{-1}, and <MDL and 988 µg L^{-1}, respectively (Fig. 21), and in the water samples collected at the Haveri and Pyhäsalmi study sites, all arsenic species' concentrations ranged between non-detected and <MDL. Because of sample dilution, the effective MDL for the Ylöjärvi samples varied. For all Haveri and Pyhäsalmi water samples, the experimentally calculated MDLs were: 0.44 µg L^{-1} for As(III), 0.70 µg L^{-1} for MMA, and 0.51 µg L^{-1} for DMA, and 1.0 µg L^{-1} for As(V). When <MDL concentrations were assumed as zero, dissolved As(III) concentrations for the Ylöjärvi samples had an arithmetic mean of 355 µg L^{-1} and a median of 12.2 µg L^{-1}, compared with 176 µg L^{-1} and 13.2 µg L^{-1} of dissolved As(V), respectively.

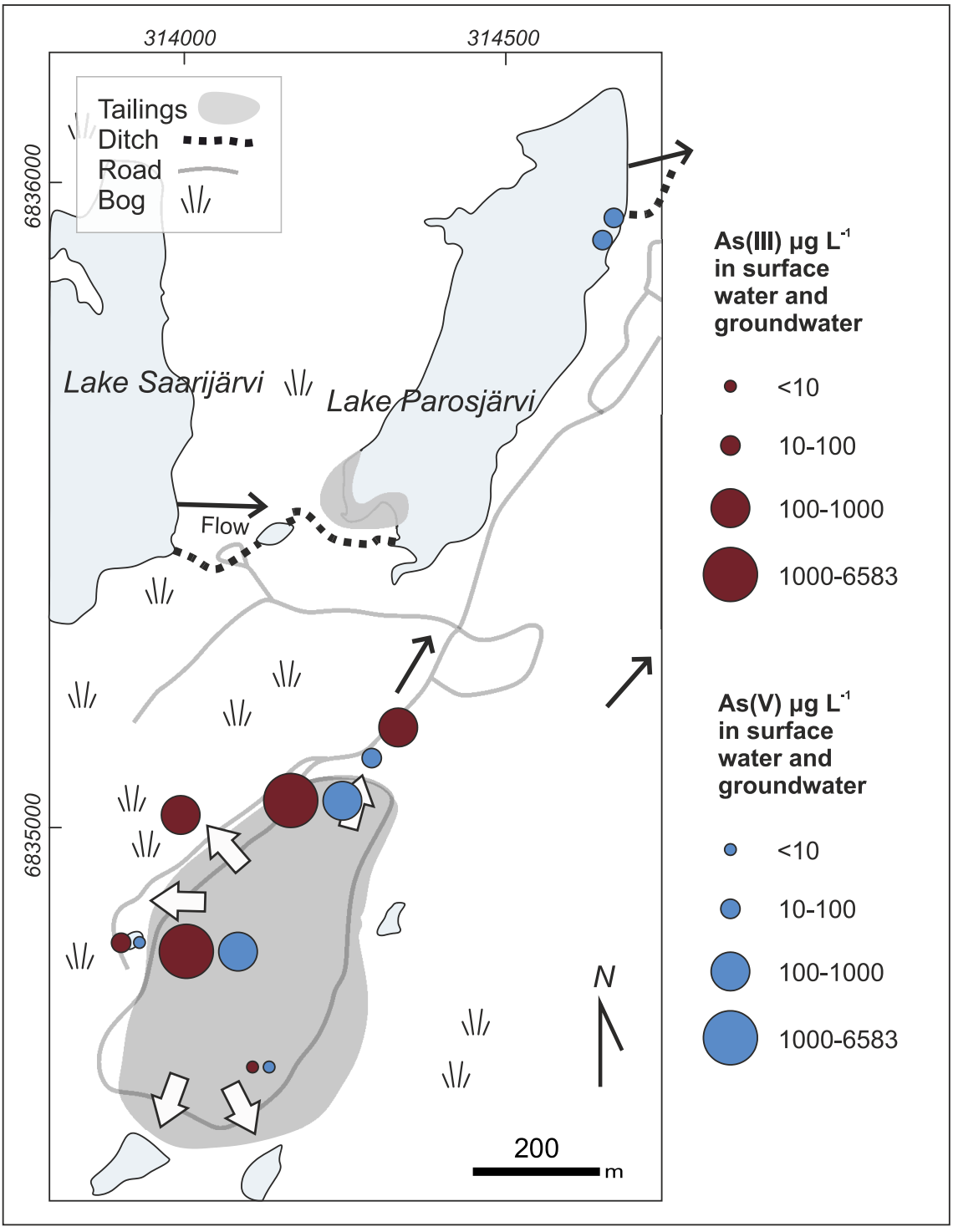

Figure 21. Dissolved As(III) and As(V) concentrations in groundwater wells and surface waters in the Ylöjärvi study area in 2019. The areal extents of the tailings deposits were modified from Carlson et al. (2002) and Parviainen et al. (2012), and the surface water flow directions, depicted as arrows, were modified from Parviainen et al. (2012) and National Land Survey of Finland (2019). Groundwater flow directions (modified from Carlson et al. 2002) are depicted as white arrows.

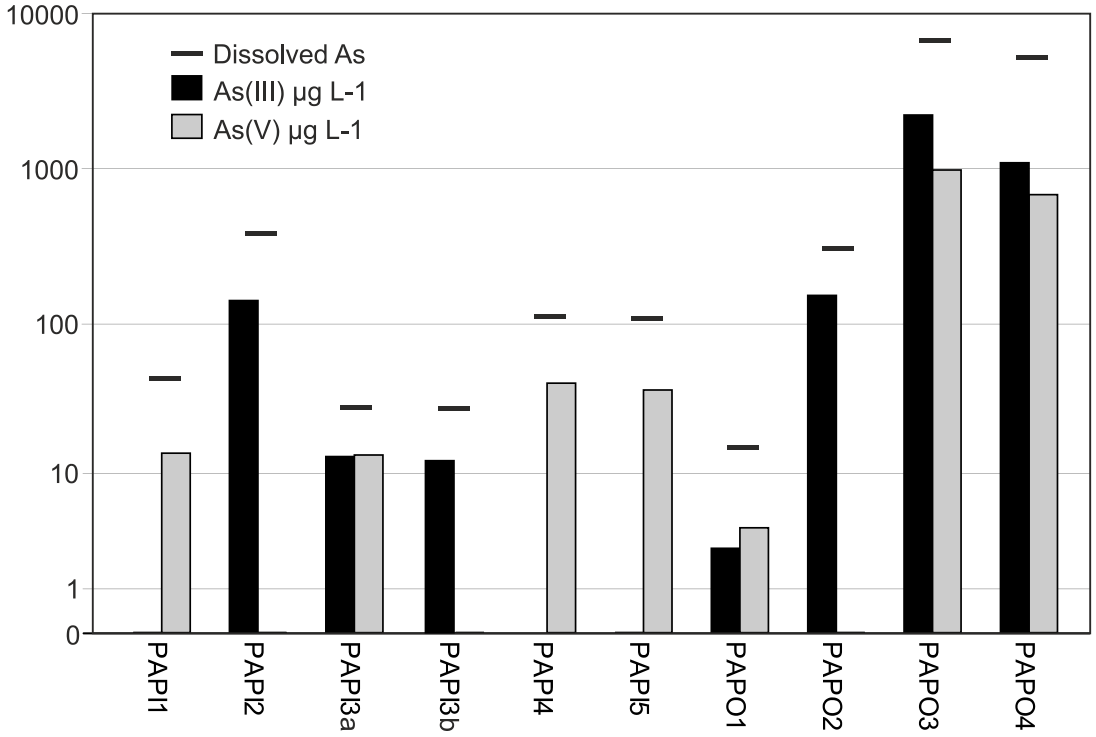

Figure 22. Total dissolved arsenic concentration and chemical speciation of arsenic [As(III) and As(V)] in water samples collected at the Ylöjärvi study area, with field duplicates PAPI3a–b included. Because of large differences between the concentrations, a logarithmic scale was used. The Haveri and Pyhäsalmi samples were not included to the figure because all their arsenic species' concentrations were below the MDLs. For locations of sample ID's see Figures 2, 5, and 8.

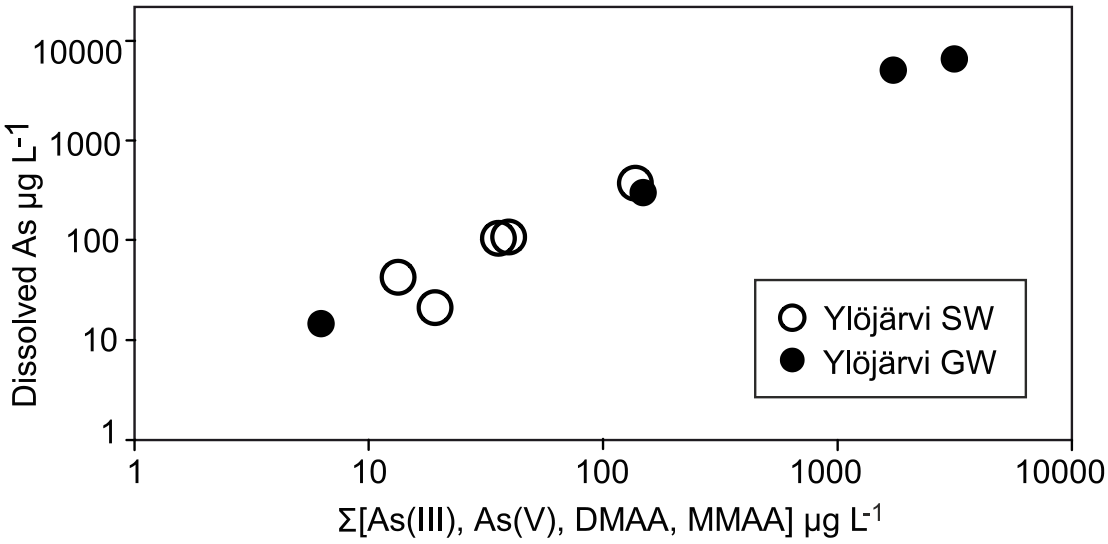

Figure 23. Relationship between the average dissolved arsenic concentrations of the HNO_3-preserved and EDTA-preserved water samples and the sum of the dissolved arsenic species concentrations (n=9; a field duplicate of two samples was merged into one using average concentrations). <MDL concentrations were assumed as zero. SW = surface water samples, GW = groundwater well samples. Haveri and Ylöjärvi samples were not included in the plot because all their speciation concentrations were below the MDLs.

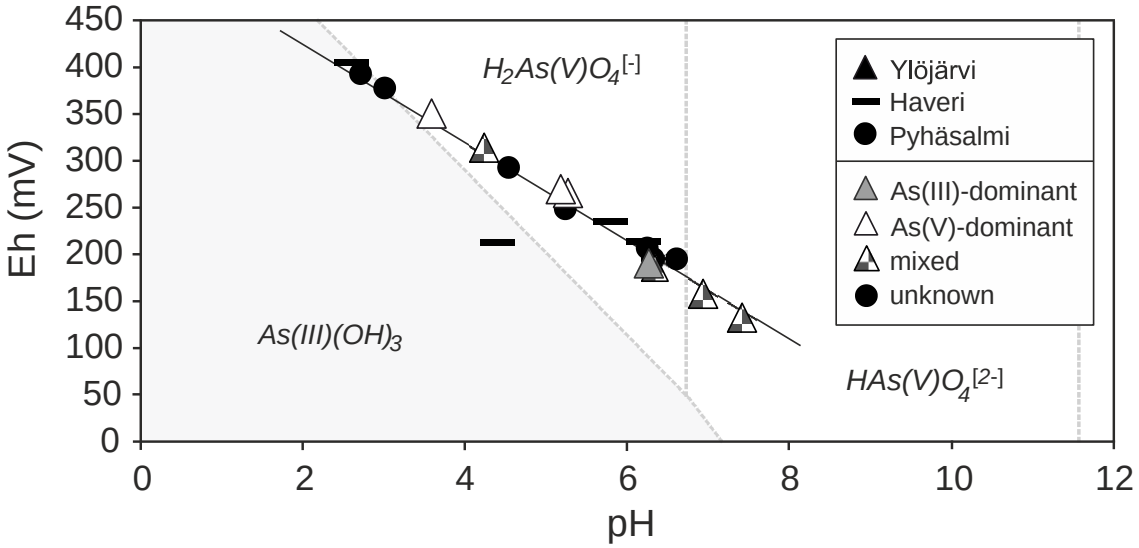

Figure 24. Eh as a function of pH of the 19 sample point field measurements in the three study areas marked with different symbols. Samples with As(III) as the dominant form of dissolved iAs are depicted as grey symbols with a black outline, samples with As(V) as the dominant form are depicted as white symbols with a black outline, and samples that had mixture of both are depicted as symbols with a grey-white pattern fill. Symbols of samples with unknown speciation ratios have a black fill. Plotted in the figure are also separate fields for species $As(III)(OH)_3$, $H2As(V)O_4^-$, and $HAs(V)O_4^{2-}$, modified from the theoretical Eh–pH diagram for aqueous arsenic species in an As–O–H system at 298.15 K, 10^5 Pa by Takeno (2005).

For the 20 waters sampled in this study, Eh and pH showed a strong negative correlation (r=-0.96**; Fig. 24). When plotted to the Eh–pH diagram, symbols representing the Eh–pH conditions of the sampled waters appear close to the $As(OH)_3/(H_2AsO_4^-/HAsO_4^{2-})$ boundary, with a majority in the $H_2AsO_4^-$ field. In the Ylöjärvi tailings groundwater well samples, the majority of iAs was As(III), but in the Ylöjärvi surface water samples near the tailings, As(III)/As(V) ratios were mixed. In the two water samples collected at northern Lake Parosjärvi, more than 90% of dissolved iAs was As(V): As(III) concentrations were below the MDLs, while As(V) concentrations were 35.7 µg L^{-1} and 39.6 µg L^{-1}.

Dissolved As(III) concentrations of the surface water field duplicates PAPI3a–b had a difference of 6.7%, but the dissolved As(V) concentrations were contrasting: PAPI3(a) had a dissolved As(V) concentration of 13.1 µg L^{-1}, while PAPI3(b) had a dissolved As(V) concentration below the MDL. Considering the relatively similar concentrations of dissolved As(III) in the field duplicates PAPI3a and PAPI3b, it is more likely that during sample collection, handling, and storage, As(V) in the sample PAPI3b had adsorbed from the solution than that it had significantly reduced to As(III).

It is also possible that the speciation analysis of the field duplicates was invalid, although, as this could not be guaranteed, the results of the field duplicates were included to the study.

In the water samples collected at the Ylöjärvi study area, the sums of the analyzed arsenic species' concentrations averaged 47.5% of the total dissolved arsenic concentration. For the samples collected at the Pyhäsalmi and Haveri study areas, exact sums of arsenic species were not determined.

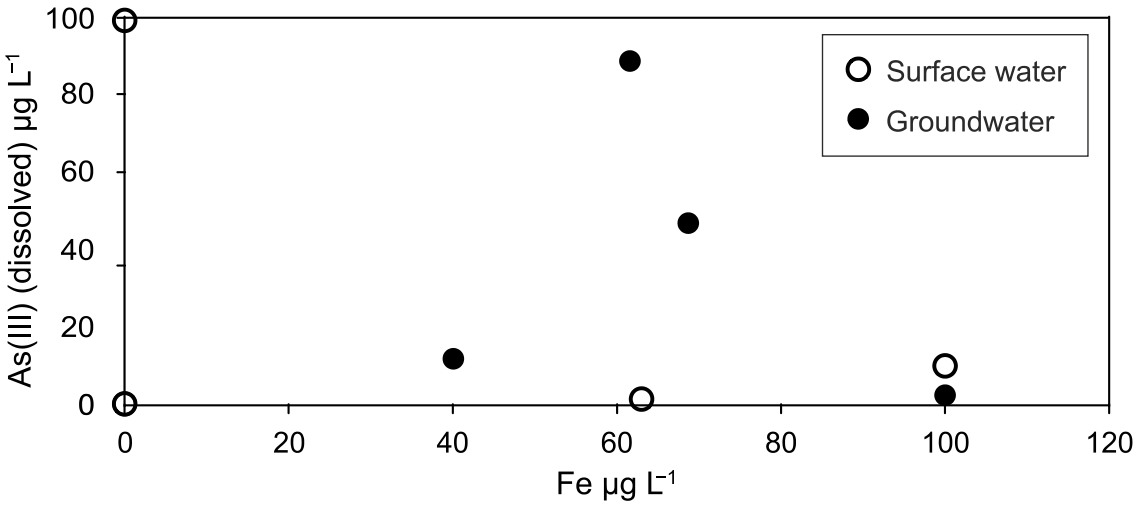

Figure 25. Relationship between As(III) percentage and Fe concentration by water type.

Dissolved As(III) showed a significant 2-tailed Pearson correlation with Mo (r=0.85**, n=9, Appendix 4), a positive correlation with K (r=0.73*, n=8), and negative correlations with Cu (r=-0.74*, n=9) and Pb (r=0.74*, n=9). Dissolved As(V) showed a positive correlation with V (r=0.78*, n=9). Dissolved As(III) (Fig. 25) and As(V) showed insignificant correlations with Fe (r=0.50, r=0.32). It must be noted that the sample size for the As(III) and As(V) correlation analyses was small.

5. DISCUSSION

5.1. Geochemistry and ionic balance

In general, in all study areas, relative to the distance from tailings, pH values increased, EC values decreased, and dissolved oxygen values were mixed. Elevated elemental concentrations were measured in surface waters in all study areas. Anomalously high maximum concentrations of dissolved Al, Ca, Co, Cu, Fe, Ni, and SO_4, compared to nation-wide data covering stream waters (Lahermo et al. 1996) and well waters (Lahermo et al. 2002), were measured in a sample collected from an Ylöjärvi study area surface water located outside the northern edge of the large tailings pile (PAPI1), in a sample collected at the Haveri study area from runoff on the NE side of the failed dam (HAPI1), and in a sample collected from a seepage collection ditch (PYPI5) at the Pyhäsalmi study area. However, concentrations measured for the samples HAPI1 and PYPI5 should be considered as possibly biased based on their ionic balance errors of -15.4% and -11.8%, as presented in Section 4.2. Nevertheless, the ionic balance errors of these levels do not change the fact that the maximum concentrations measured for these samples were anomalously high.

Regarding groundwater samples, at the large Ylöjärvi study area tailings pile, anomalously high concentrations were measured for dissolved Ca (45.7 to 233 mg L^{-1}), Fe (2.6 to 88.8 mg L^{-1}), SO_4 (46.8 to 680 mg L^{-1}), and arsenic, as presented in Section 4.3. Based on contaminant concentrations in the surface water samples collected at the Ylöjärvi study area, groundwater in the large Ylöjärvi tailings pile seeps to the west and to the north, although, the sample PAPI1, collected outside the northern edge of the tailings, had also higher contaminant concentrations than any of the groundwater well samples collected at the large tailings pile. Carlson et al. (2002) reported groundwater in the large Ylöjärvi tailings pile seeping to the south, west, and north, transporting contaminants to the surrounding environment. Carlson et al. (2002) also reported notable seeping of groundwater in the NW part of the large Ylöjärvi tailings, with seepage and runoff flowing into a severely contaminated wetland, in where the sampling point PAPI2 of this study is located. In sample PAPI2, elevated concentrations,

compared to nation-wide data covering stream waters (Lahermo et al. 1996), were measured for dissolved arsenic, Co, Fe, Mn, and Mo.

Conditions in the surface waters sampled in the Ylöjärvi study area were, in general, more oxidizing than in the groundwater wells located in the large tailings pile. Also, regarding groundwater samples, anomalously high concentrations were measured in the Pyhäsalmi groundwater monitoring well sample PYPO3, a groundwater monitoring well located some 100 m SW of the Pyhäsalmi tailings, for dissolved Ca (124 mg L^{-1}), Mg (101 mg L^{-1}), Ni (45.9 µg L^{-1}), and SO_4 (778 mg L^{-1}), indicating groundwater contamination from tailings, however, the dissolved arsenic concentration of the sample was in the natural background range. The sample from the groundwater monitoring well PYPO2 at the Pyhäsalmi study area, located further away from the tailings than PYPO3, did not show as high values as PYPO3, although concentrations of, e.g., Fe (4.1 mg L^{-1}) and SO_4 (129 mg L^{-1}) were elevated compared to natural background values. The sample collected at the shore of Lake Pyhäjärvi had mostly similar elemental concentrations as the values reported for Lake Pyhäjärvi by Räisänen and Mäkinen (2007).

Almost all dissolved concentrations measured for the samples collected at the Haveri study area showed a distinct decrease from the tailings to the surroundings, a result which is in line with previous results reported by Valo (2012). At the Haveri tailings pile, Valo (2012) reported groundwater and surface water flowing to the NE, a flow direction that was also observed for runoff in this study. In Haveri, as pH in the tailings pile remains low, metals continue to dissolve in surface water and groundwater. Almost all dissolved concentrations measured in the tailings sedimentation basin water sample HAPI3 were larger than those measured on the Lake Kirkkojärvi side of the dam in sample HAPI4. HAPI4 sample concentrations were all in the same range as Lake Kirkkojärvi concentrations reported by Valo (2012). These results indicate that the dam between the tailings sedimentation basin and Lake Kirkkojärvi is effective in blocking contaminants from seeping into the lake.

The lake water and tailings sedimentation basin water samples not diluted for ion chromatography analysis had an IB error of 0.8 to 3.6% with an arithmetic mean of 2.4%, while all other samples, diluted for IC analysis for all ions except Cl, had an IB error percentage of 0.0 to 15.4%, with an arithmetic mean of 5.1%, when calculated with all

error percentages as positive percentage values. Therefore, it is possible that the dilution of the samples for the IC analysis caused an increase in the IB error.

5.2. Arsenic occurrence

5.2.1. Ylöjärvi study area

All water samples collected at the Ylöjärvi study area had dissolved arsenic concentrations above the maximum contaminant level (MCL) of 10 µg L^{-1} in drinking water and household water (FMSAH 1994, FMSAH 2015). Dissolved arsenic concentrations in the Ylöjärvi study area groundwater well and surface water samples measured in this study were notably higher than the natural background of local stream waters: Tarvainen and Mannio (2004) reported natural stream waters closer than about 50 km from the Ylöjärvi study area ranging between 0.4 µg L^{-1} and 5.0 µg L^{-1} arsenic; and, generally larger than concentrations of the local bedrock wells. Drilled bedrock wells near the area have elevated arsenic concentrations compared to average Finnish bedrock wells. Some bedrock wells reported by Backman et al. (2006) located less than about 5 km from the abandoned mine had >50 µg L^{-1} arsenic.

The dissolved arsenic concentrations measured in this study were mostly in the same range as previous measurements from the same site and somewhat similar sampling points reported by Carlson et al. (2002) and Parviainen et al. (2012), suggesting continued and long-term dissolution of arsenic from arsenic-bearing sulfide minerals in the former Ylöjärvi mine tailings being exposed to an oxidizing environment. Carlson et al. (2002) reported dissolved arsenic concentrations measured in the Ylöjärvi study area surface waters ranging between 3.89 and 3440 µg L^{-1}, and the dissolved arsenic concentrations measured in groundwater monitoring wells in or near the tailings pile ranging between 50.4 and 10100 µg L^{-1}. Parviainen et al. (2012) reported high dissolved arsenic concentrations in the groundwater monitoring wells ranging between 4740 and 14500 µg L^{-1}.

As previously discussed in Section 5.1, groundwater at the large Ylöjärvi tailings pile is seeping to the south, west, and north, which can be seen in, e.g., the high dissolved arsenic concentrations, with an average of 374 µg L^{-1}, in the wetland water sample PAPI2 located west of the large tailings pile. Dissolved arsenic concentrations were higher in the wetland sample PAPI2 than in the Parosjärvi samples, but lower in the surface water samples PAPI1 and PAPI3 than in the Parosjärvi samples PAPI4 and PAPI5. However, the dissolved arsenic concentration in the groundwater well sample PAPO2, at a distance of about 10 m from the PAPI1 surface water sampling point, had a dissolved arsenic concentration of 300 µg L^{-1} compared with 42.6 µg L^{-1} in PAPI1, and 105–108 µg L^{-1} in PAPI4–5.

The samples indicate more neutral pH conditions in the waters of the groundwater monitoring wells than in the nearby surface waters. In the acidic to slightly acidic waters from which the surface water samples were collected, the concentrations of dissolved arsenic were lower compared with, e.g., Co, Cu, Zn, and Ni, and therefore, in these acidic conditions, arsenic is probably adsorbed on Fe oxides, while Co, Cu, Zn, and Ni are dissolved.

Regarding natural background levels of arsenic in till, in central Pirkanmaa, where both the Ylöjärvi and Haveri study areas are located, Koljonen (1992) reported total arsenic concentrations in fine fraction of till (< 0.06 mm) of 4–7 mg kg^{-1}, and the national soil database TAPIR (Jarva et al. 2010) showed an average of 9.43 mg kg^{-1} and a median of 6.9 mg kg^{-1} arsenic in a <2 mm fraction of till. In sequential extractions of the tailings, Parviainen et al. (2012) reported an average arsenic concentration of 2615 mg kg^{-1}.

The sampled waters with the highest levels of contamination are located in a restricted military area. In this study, and, in general, in previous studies by, e.g., Carlson et al. (2002), dissolved arsenic concentrations in Lake Parosjärvi have been about 10-fold the MCL for arsenic in drinking water and household water, however, it must be noted that Lake Parosjärvi water is not used as drinking water. Public access to Lake Parosjärvi is not restricted, but at spots around Lake Parosjärvi, there are warning signs in place.

5.2.2. Haveri study area

All water samples collected at the Haveri study area had dissolved arsenic concentrations below the MCL of 10 µg L^{-1} for arsenic in drinking water and household water. In this study, the maximum dissolved arsenic concentration in the Haveri study area, 6.2 µg L^{-1}, was more than double the maximum arsenic concentration documented in previous studies by Valo (2012) and Parviainen (2009): Valo (2012) reported dissolved arsenic concentrations measured in surface waters in the vicinity of the Haveri tailings ranging between 0.3 and 2.1 µg L^{-1}, and Parviainen (2009) reported dissolved arsenic concentrations measured in surface waters in the Haveri tailings, and in the vicinity of the Haveri tailings, ranging between 0.3 and 2.3 µg L^{-1}. This indicates continuing dissolution of arsenic from the tailings also in the Haveri study area, although at a much smaller scale than in the Ylöjärvi study area. In runoff, arsenic, along with other contaminants, moves to the NE as the tailings pile slopes towards Lake Kirkkojärvi.

Tarvainen and Mannio (2004) reported natural stream waters located closer than 50 km from the study area ranging between 0.3 and 5.0 µg L^{-1} arsenic. In the study of Backman et al. (2006), no bedrock wells located at a distance of less than about 15 km from the Haveri study area exceeded 10 µg L^{-1} arsenic, and, Parviainen (2009) reported dissolved arsenic concentrations measured in a groundwater well about 700 m west from the Haveri tailings ranging between 0.1 and 0.2 µg L^{-1}. Parviainen (2009) reported aqua regia leaching of the tailings showing total arsenic concentrations of 29–510 mg kg^{-1}, which are notably less than the average arsenic concentration in the tailings at the Ylöjärvi study area.

5.2.3. Pyhäsalmi study area

Similar to water samples collected at the Haveri study area, all samples collected at the Pyhäsalmi study area had dissolved arsenic concentrations below the MCL for arsenic in drinking water and household water. Dissolved arsenic concentrations in surface waters and tailings seepage ditch collection waters at the Pyhäsalmi study area were generally in the same range as previous arsenic concentrations reported by Räisänen and Skinnari (2015). Tarvainen and Mannio (2004) reported four natural stream waters located closer

than about 40 km from the Pyhäsalmi mine study area having between 0.5 µg L^{-1} and 1.2 µg L^{-1} arsenic. Räisänen and Skinnari (2015) reported dissolved arsenic concentrations measured in natural surface waters in Pyhäsalmi mine and its vicinity ranging between 0.4 and 2.5 µg L^{-1}.

Water from the tailings area flows mainly west towards Lake Pyhäjärvi (126 km^2), for which Räisänen and Mäkinen (2007) reported total arsenic concentrations in 71 water samples ranging between 0.3 and 1.6 µg L^{-1}. Regarding groundwater, Räisänen and Skinnari (2015) documented a dissolved arsenic concentration of 17 µg L^{-1} in a Pyhäsalmi mine groundwater sample about 200 m SW of the tailings pile, while in this study, dissolved arsenic concentrations in the Pyhäsalmi groundwater samples, collected from different groundwater wells than in Räisänen and Skinnari (2015), were only 0.2–0.4 µg L^{-1}, and were thus even smaller than the average dissolved arsenic concentrations measured in natural surface waters in the Pyhäsalmi mine and its vicinity by Räisänen and Skinnari (2015).

As an example of natural background level measurements of arsenic in till, in the vicinity of the Pyhäsalmi study area, Koljonen (1992) reported total arsenic concentrations in fine fraction of till (< 0.06 mm) of 3–5 mg kg^{-1}. Arsenic concentration data was not available for areas close to the Pyhäsalmi mine in the national soil database TAPIR (Jarva et al. 2010). Toropainen and Heikkinen (2006) reported XRF analysis and aqua regia leaching of tailings samples showing total arsenic concentrations of 386 and 367 mg kg^{-1}, respectively, which are notably less than the average arsenic concentration in the tailings at the Ylöjärvi study area, and in the same range as the arsenic concentrations measured in the tailings at the Haveri study area.

5.2.4. Correlations

Dissolved arsenic concentrations were compared to several dissolved elemental concentrations and physicochemical parameters that may control or affect arsenic occurrence in the mining-impacted areas studied. Correlation results suggest that in the selected study areas, dissolved arsenic and Mo occurrence may be controlled by the same environmental variables, and that dissolved Mo can be an indicator of dissolved arsenic

concentrations. The significant 2-tailed Pearson correlation of dissolved arsenic with dissolved Mo (r=0.80**) found for the concentrations measured in this study is in line with a previous study of Finnish well waters by Lahermo et al. (2002) reporting a significant Pearson correlation of arsenic only with Mo (r=0.41**, n=263), and, as well as a previous bedrock well study by Juntunen et al. (2004) in Pirkanmaa, Finland, reporting arsenic correlating most strongly with Mo.

In this study, dissolved arsenic also correlated with dissolved K (r=0.68**) and dissolved Cl (r=-0.51*). These less significant correlations, as well as a review of the concentration results show that, in this study, dissolved K and Cl concentrations are not as good an indicator of dissolved arsenic concentrations as dissolved Mo. Dissolved arsenic also showed an insignificant correlation with dissolved Fe, but, when the correlation analysis was run excluding the Ylöjärvi water samples, dissolved arsenic showed a significant positive correlation with Fe; thus, in the Pyhäsalmi and Haveri study areas, dissolved Fe may be a good indicator of dissolved arsenic.

5.3. Arsenic speciation

In the Ylöjärvi study area, the samples that had the largest dissolved arsenic concentrations were predominantly dissolved As(III) (Fig. 19). These samples were collected at the western and northern parts of the large tailings pile, and in the wetland west of the large tailings pile. Further away from the tailings, in northern Lake Parosjärvi, the samples had 35–40 µg L^{-1} As(V), while As(III) concentrations were below the MDL. The dominance of As(V) in water samples collected at Lake Parosjärvi can be compared with previous arsenic speciation analyses by Carlson et al. (2002), which showed, e.g., that in an Ylöjärvi tailings seepage water sample 19.3% of iAs was As(III), then, in a water sample collected from a ditch at about 100 m from the tailings, flowing to Lake Parosjärvi, 96% of arsenic was As(V), and, at about 300 m distance from the tailings, 99% of analyzed arsenic was As(V). There was a maximum difference between the reported filtered arsenic concentration and the sum of all arsenic species concentrations of about 20%, compared with 68.6% in this study. Arsenic speciation was analyzed in this study using HPLC-ICP-MS and filtered EDTA-preserved samples, while Carlson et

al. (2002) analyzed arsenic speciation using a method based on ion exchange and filtered samples with HNO_3 as a preservative.

Parviainen et al. (2012) demonstrated that in 13 out of 13 Ylöjärvi mine tailings pore water samples and in two out of two groundwater samples, As(III) concentrations were very low according to thermodynamic calculations with PHREEQC software. These results differ from the results presented in this study, the most likely reason for which are significant differences in sample collection, preservation, and analysis methods.

Adsorption studies on Fe oxides have shown that adsorption of As(V) increases with decreasing pH, reaching the maximum level of adsorption in low pH conditions, whereas As(III) adsorption does not increase with decreasing pH (Dixit and Hering 2003, Campbell and Nordstrom 2014). In this study, regarding iAs, the water samples with the lowest pH values were either As(V)-dominant or mixed. As(III) concentrations showed a positive correlation with pH ($r=0.76^*$, $n=8$), and a negative correlation with Eh ($r=-0.76^*$, $n=8$), while As(V) concentrations did not show significant correlations with any physicochemical measurements. The relationship between the As(III) percentage and dissolved Fe concentration showed no clear pattern. Based on the theoretical Eh–pH diagram for aqueous arsenic species by Takeno (2005), in As–O–H systems, the majority of arsenic in the samples of this study would be As(V). In this study, the sampled waters represent more complex systems than simply an As–O–H system, and as presented in Section 4.3.2., the majority of arsenic in the samples was not As(V).

As mentioned in Section 3.2.3., in a perfect analysis, if 100% of the dissolved arsenic in the water samples consisted of As(III), As(V), DMA and MMA, the sum of the species' concentrations and the total dissolved arsenic concentration would equal. The observed percentage of identified arsenic species in this study may result from, e.g., adsorption of arsenic in the water samples, or, notable quantities of other arsenic species present in the solutions. Since the EDTA-preserved water samples were analyzed for both total dissolved arsenic and arsenic speciation 13–14 weeks after sample collection it is not likely that a in between the two analyzes a large part of dissolved arsenic in the samples analyzed for arsenic speciation, when compared with the samples analyzed for total dissolved arsenic, would have been adsorbed.

In the water samples analyzed in this study, arsenic species may have reacted with metals during speciation analysis. As(V) can react with other metallic species to form precipitates, and also, during analysis, weakly anionic As(III) as arsenite is eluted fast from an anion exchange column near where cationic or neutral arsenic compounds elute (Day et al. 2002). An estimate of method precision was given by the RSDs obtained for a triplicate standard solution sample containing 5 µg L^{-1} of each arsenic specie (Appendix 1). The arsenic speciation recoveries (n=6) obtained for standard solution samples ranged between 90% and 98% (Appendix 1). In order to identify other possible arsenic species present in the water samples, new methods would have to be used.

5.4. Suggestions for future studies

As presented in Section 4.3.2., the sums of the analyzed arsenic species' concentrations averaged 47.5% of total dissolved arsenic in the water samples collected at the Ylöjärvi study area, while in the water samples collected at the Pyhäsalmi and Haveri study areas all arsenic species remained unidentified. Considering the levels of the MDLs, e.g., in the seepage collection ditch sample PYPI5 in Pyhäsalmi, which had 8.6 µg L^{-1} dissolved arsenic, possibly over 70% of dissolved arsenic in the sample consisted of species unidentified by the used analysis method. Identification of dissolved arsenic species in the waters sampled at the Haveri and Pyhäsalmi study sites, as well as identification of MMA and DMA in all waters sampled could be improved by enhancing the used analytical method by, e.g., using larger amounts of EDTA per sample in order to chelate metal cations more effectively, or, by using other analytical approaches. Also, the extent to which different arsenic species are controlled directly by geochemical or physicochemical parameters or conditions in the studied mining-impacted environments requires more detailed study.

6. CONCLUSIONS

Anomalously high maximum concentrations of Al, Ca, Co, Cu, Fe, Ni, and SO_4, compared with natural background, were measured in surface water samples collected at the Ylöjärvi and Haveri study areas, and in a seepage collection ditch sample collected at the Pyhäsalmi study area. High arsenic concentrations were measured in groundwater and surface water in the Ylöjärvi study area surrounding the tailings of the former Ylöjärvi Cu–W–As mine. Continuing dissolution of arsenic from the tailings at the Ylöjärvi study area leads to arsenic release to the surroundings. All dissolved arsenic concentrations in the study areas surrounding the tailings of the former Haveri Au–Cu mine and the active Pyhäsalmi Zn–Cu mine were below the Finnish maximum contaminant level of 10 µg L^{-1} for arsenic in drinking water and household water.

Of the water samples collected at the Ylöjärvi study site, two samples had dissolved arsenite [As(III)] as the dominant dissolved inorganic arsenic (iAs) specie, three had dissolved arsenate [As(V)] as the dominant iAs specie, while four samples had a mixture of both species. Water samples containing high concentrations of arsenic generally contained more As(III) than As(V).

Concentrations of all analyzed dissolved arsenic species in the water samples collected at the Haveri and Pyhäsalmi study areas were below the MDLs, and the concentrations of both MMA and DMA were below the MDLs in all water samples in this study. A close correlation result between arsenic and Mo suggests that, in general, in the sampled waters and their surrounding environments, arsenic and Mo distributions are controlled by the same environmental variables.

In the water samples collected at the Ylöjärvi study area, the sums of the measured arsenic species' concentrations averaged 47.5% of total dissolved arsenic concentration. Identification of other arsenic species dissolved in the sampled waters requires more detailed study. The findings of the geochemical and physicochemical measurements of this study contribute to improve knowledge about arsenic occurrence and mobility, as well as arsenic speciation in tailings environments.

7. ACKNOWLEDGEMENTS

First, I would like to thank my supervisors Juhani Virkanen and Seija Kultti for allowing me to pursue challenging scientific problems while providing expertise and support. I would like to thank Hanna Reijola for the guidance and help in the lab, Kirsi Sundell and Maria Hänninen for making my field work possible, and fellow students for the collegiality. I was fortunate to receive funding: I would like to thank both the Finnish Society for Soil Investigation and Remediation (MUTKU ry) and the Master's Programme in Geology and Geophysics for providing me with funding. Finally, I want to thank my family for their love and support.

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APPENDICES

Appendix 1

Table 1. RSD percentages and standard deviations of the triplicate standard solution samples containing 5 µg L^{-1} of each arsenic specie.

Sample	75 As(III)	75 DMA	75 MMAA	75 As(V)
1	4.999	4.843	5.029	4.919
2	4.843	4.882	4.841	4.693
3	4.711	4.789	4.88	4.763
Average	4.85	4.84	4.92	4.79
S.D.	0.14	0.05	0.10	0.12
RSD (%)	2.97	0.97	2.02	2.41

S.D. = standard deviation

Table 2. Recoveries obtained for arsenic species in samples analyzed in the sample batch before and after the mining-impacted water samples.

Before				
	75 As(III)	75 DMAA	75 MMAA	75 As(V)
Concentration	<0.440	<0.510	<0.700	2.889
Sample+6.5 ppb	6.294	6.199	6.364	8.866
Net	6.294	6.119	6.364	5.977
Recovery (%)	97	94	98	92

After				
	75 As(III)	75 DMAA	75 MMAA	75 As(V)
Concentration	<0.440	<0.510	<0.700	2.277
Sample+6.5 ppb	5.887	5.925	5.829	8.468
Net	5.887	5.925	5.829	6.191
Recovery (%)	91	91	90	95

Appendix 2

Table 1. Relative standard deviation (RSD) percentages of the ion chromatography triplicate samples and the yield percentage range for the aqueous constituents of the VKI certified reference material.

Sample	Na	K	Ca	Mg	F	Cl	SO4	Yield (%)
VKI_Reference	0.16	0.40	0.15	0.55	2.74	0.17	1.06	98.0–103.7
PAPI3_20x	2.00	2.79	2.38	4.27	5.00	–	1.83	
HAPI2_20x	8.89	10.98	8.50	8.63	13.48	1.72	1.22	
PYPO3_20x	4.25	na	4.47	4.61	26.45	0.58	1.11	
HAPI1_100x	4.09	–	6.67	7.36	5.54	–	4.33	

na = not analyzed because concentrations were below detection
– = triplicate sample concentration results were not included in the study because of more accurate available data from less diluted aliquots

Appendix 3

Table 1. Results of the Shapiro-Wilk test of normality. If p>0.05, normality can be assumed. Base-10 log-transformed measurements and concentrations were marked with an asterisk (*).

	W	n	p
pH (field)	0.933	19	0.195
Eh mV	0.932	19	0.190
*EC µS cm-1	0.918	19	0.106
DO mg L-1	0.862	19	0.011
*As	0.907	19	0.066
*Cd	0.955	19	0.474
*Co	0.980	19	0.941
*Cr	0.901	19	0.051
*Cu	0.935	19	0.217
*Mo	0.905	19	0.060
*Ni	0.922	19	0.122
*P	0.913	19	0.085
*Pb	0.975	19	0.877
*Se	0.921	19	0.117
*Si	0.951	19	0.412
*V	0.974	19	0.859
*U	0.928	19	0.157
*Al	0.884	19	0.026
*Ca	0.883	19	0.025
*Fe	0.931	19	0.179
*K	0.923	19	0.130
*Mg	0.963	19	0.628
*Mn	0.927	19	0.150
*Na	0.936	19	0.220
*Zn	0.946	19	0.339
*Cl	0.769	19	0.000
*HCO3	0.940	12	0.500
*SO4	0.951	19	0.408

W = correlation between an ideal normal distribution and the measurement results
n = number of samples
p = significance level

Appendix 4

Table 1. Pearson correlation coefficients for variables pH–Pb included to the statistical analyses. 2-tailed correlations significant at the 0.01 level were marked with two asterisks (**) and a gray text highlight, and 2-tailed correlations significant at the 0.05 level were marked with one asterisk (*).

		pH (field)	Eh	EC	DO	As	As (HNO3)	As (EDTA)	As(III)	As(V)	Cd	Co
pH (field)	Corr.	1	-,962**	-,514*	0,140	0,232	0,229	0,235	,756*	0,446	-,874**	-,748**
	Sig.		0,000	0,024	0,567	0,340	0,346	0,333	0,030	0,268	0,000	0,000
	N	19	19	19	19	19	19	19	8	8	19	19
Eh	Corr.	-,962**	1	0,426	-0,029	-0,217	-0,214	-0,221	-,764*	-0,389	,842**	,676**
	Sig.	0,000		0,069	0,906	0,372	0,380	0,362	0,027	0,340	0,000	0,001
	N	19	19	19	19	19	19	19	8	8	19	19
EC	Corr.	-,514*	0,426	1	-,560*	0,118	0,122	0,113	0,530	-0,059	0,454	,759**
	Sig.	0,024	0,069		0,013	0,631	0,618	0,645	0,177	0,889	0,051	0,000
	N	19	19	19	19	19	19	19	8	8	19	19
DO	Corr.	0,140	-0,029	-,560*	1	-0,339	-0,341	-0,333	-0,307	0,331	0,058	-,507*
	Sig.	0,567	0,906	0,013		0,156	0,153	0,163	0,460	0,424	0,812	0,027
	N	19	19	19	19	19	19	19	8	8	19	19
As	Corr.	0,232	-0,217	0,118	-0,339	1	,999**	,999**	,861**	0,651	-0,411	0,262
	Sig.	0,340	0,372	0,631	0,156		0,000	0,000	0,003	0,058	0,072	0,264
	N	19	19	19	19	20	20	20	9	9	20	20
As (HNO3)	Corr.	0,229	-0,214	0,122	-0,341	,999**	1	,997**	,854**	0,619	-0,410	0,260
	Sig.	0,346	0,380	0,618	0,153	0,000		0,000	0,003	0,076	0,073	0,268
	N	19	19	19	19	20	20	20	9	9	20	20
As (EDTA)	Corr.	0,235	-0,221	0,113	-0,333	,999**	,997**	1	,859**	,687*	-0,411	0,265
	Sig.	0,333	0,362	0,645	0,163	0,000	0,000		0,003	0,041	0,072	0,260
	N	19	19	19	19	20	20	20	9	9	20	20
As(III)	Corr.	,756*	-,764*	0,530	-0,307	,861**	,854**	,859**	1	0,352	-0,547	-0,212
	Sig.	0,030	0,027	0,177	0,460	0,003	0,003	0,003		0,352	0,127	0,584
	N	8	8	8	8	9	9	9	9	9	9	9
As(V)	Corr.	0,446	-0,389	-0,059	0,331	0,651	0,619	,687*	0,352	1	-0,066	-0,199
	Sig.	0,268	0,340	0,889	0,424	0,058	0,076	0,041	0,352		0,867	0,608
	N	8	8	8	8	9	9	9	9	9	9	9
Cd	Corr.	-,874**	,842**	0,454	0,058	-0,411	-0,410	-0,411	-0,547	-0,066	1	,621**
	Sig.	0,000	0,000	0,051	0,812	0,072	0,073	0,072	0,127	0,867		0,003
	N	19	19	19	19	20	20	20	9	9	20	20
Co	Corr.	-,748**	,676**	,759**	-,507*	0,262	0,260	0,265	-0,212	-0,199	,621**	1
	Sig.	0,000	0,001	0,000	0,027	0,264	0,268	0,260	0,584	0,608	0,003	
	N	19	19	19	19	20	20	20	9	9	20	20
Cr	Corr.	-,646**	,625**	,570*	0,110	-0,212	-0,207	-0,215	-0,082	0,653	,640**	0,416
	Sig.	0,003	0,004	0,011	0,655	0,369	0,381	0,364	0,834	0,057	0,002	0,068
	N	19	19	19	19	20	20	20	9	9	20	20
Cu	Corr.	-,937**	,923**	0,343	0,100	-0,406	-0,411	-0,400	-,735*	-0,194	,931**	,631**
	Sig.	0,000	0,000	0,150	0,684	0,075	0,072	0,080	0,024	0,618	0,000	0,003
	N	19	19	19	19	20	20	20	9	9	20	20
Mo	Corr.	,621**	-,564*	-0,137	-0,089	,802**	,802**	,801**	,851**	0,588	-,699**	-0,228
	Sig.	0,005	0,012	0,576	0,718	0,000	0,000	0,000	0,004	0,096	0,001	0,333
	N	19	19	19	19	20	20	20	9	9	20	20
Ni	Corr.	-,859**	,774**	,727**	-0,310	-0,140	-0,140	-0,140	-0,372	-0,204	,804**	,846**
	Sig.	0,000	0,000	0,000	0,196	0,555	0,556	0,556	0,325	0,599	0,000	0,000
	N	19	19	19	19	20	20	20	9	9	20	20
P	Corr.	-,627**	,541*	,564*	0,004	-0,330	-0,325	-0,334	-0,459	-0,401	,533*	,472*
	Sig.	0,004	0,017	0,012	0,987	0,156	0,163	0,151	0,214	0,284	0,016	0,036
	N	19	19	19	19	20	20	20	9	9	20	20
Pb	Corr.	-,845**	,856**	0,291	0,230	-0,339	-0,348	-0,328	-,742*	0,005	,824**	,524*
	Sig.	0,000	0,000	0,227	0,343	0,143	0,133	0,158	0,022	0,990	0,000	0,018
	N	19	19	19	19	20	20	20	9	9	20	20

Table 1. – (continued)

		Cr	Cu	Mo	Ni	P	Pb	Se	Si	V	U	Al
pH	Corr.	-.646**	-.937**	.621**	-.859**	-.627**	-.845**	-.852**	-.605**	-0.365	-.703**	-.944**
(field)	Sig.	0.003	0.000	0.005	0.000	0.004	0.000	0.000	0.006	0.125	0.001	0.000
	N	19	19	19	19	19	19	19	19	19	19	19
Eh	Corr.	.625**	.923**	-.564*	.774**	.541*	.856**	.801**	.495*	0.338	.678**	.912**
	Sig.	0.004	0.000	0.012	0.000	0.017	0.000	0.000	0.031	0.157	0.001	0.000
	N	19	19	19	19	19	19	19	19	19	19	19
EC	Corr.	.570*	0.343	-0.137	.727**	.564*	0.291	.655**	.794**	0.400	.669**	.571*
	Sig.	0.011	0.150	0.576	0.000	0.012	0.227	0.002	0.000	0.090	0.002	0.011
	N	19	19	19	19	19	19	19	19	19	19	19
DO	Corr.	0.110	0.100	-0.089	-0.310	0.004	0.230	-0.257	-.525*	0.095	-0.294	-0.133
	Sig.	0.655	0.684	0.718	0.196	0.987	0.343	0.289	0.021	0.700	0.223	0.588
	N	19	19	19	19	19	19	19	19	19	19	19
As	Corr.	-0.212	-0.406	.802**	-0.140	-0.330	-0.339	-0.013	-0.125	0.153	0.176	-0.221
	Sig.	0.369	0.075	0.000	0.555	0.156	0.143	0.957	0.599	0.520	0.458	0.350
	N	20	20	20	20	20	20	20	20	20	20	20
As	Corr.	-0.207	-0.411	.802**	-0.140	-0.325	-0.348	-0.017	-0.116	0.158	0.170	-0.222
(HNO3)	Sig.	0.381	0.072	0.000	0.556	0.163	0.133	0.945	0.626	0.506	0.474	0.347
	N	20	20	20	20	20	20	20	20	20	20	20
As	Corr.	-0.215	-0.400	.801**	-0.140	-0.334	-0.328	-0.008	-0.135	0.151	0.182	-0.218
(EDTA)	Sig.	0.364	0.080	0.000	0.556	0.151	0.158	0.972	0.570	0.525	0.442	0.355
	N	20	20	20	20	20	20	20	20	20	20	20
As(III)	Corr.	-0.082	-.735*	.851**	-0.372	-0.459	-.742*	-0.348	-0.242	0.267	0.130	-0.554
	Sig.	0.834	0.024	0.004	0.325	0.214	0.022	0.358	0.530	0.487	0.740	0.121
	N	9	9	9	9	9	9	9	9	9	9	9
As(V)	Corr.	0.653	-0.194	0.588	-0.204	-0.401	0.005	0.057	-0.341	.779*	0.575	-0.075
	Sig.	0.057	0.618	0.096	0.599	0.284	0.990	0.884	0.369	0.013	0.105	0.849
	N	9	9	9	9	9	9	9	9	9	9	9
Cd	Corr.	.640**	.931**	-.699**	.804**	.533*	.824**	.816**	.528*	0.286	.670**	.940**
	Sig.	0.002	0.000	0.001	0.000	0.016	0.000	0.000	0.017	0.221	0.001	0.000
	N	20	20	20	20	20	20	20	20	20	20	20
Co	Corr.	0.416	.631**	-0.228	.846**	.472*	.524*	.859**	.598**	0.320	.752**	.767**
	Sig.	0.068	0.003	0.333	0.000	0.036	0.018	0.000	0.005	0.169	0.000	0.000
	N	20	20	20	20	20	20	20	20	20	20	20
Cr	Corr.	1	.570**	-0.319	.570**	.765**	.623**	.584**	.640**	.815**	.647**	.686**
	Sig.		0.009	0.171	0.009	0.000	0.003	0.007	0.002	0.000	0.002	0.001
	N	20	20	20	20	20	20	20	20	20	20	20
Cu	Corr.	.570**	1	-.711**	.801**	.531*	.916**	.811**	0.423	0.259	.620**	.926**
	Sig.	0.009		0.000	0.000	0.016	0.000	0.000	0.063	0.270	0.004	0.000
	N	20	20	20	20	20	20	20	20	20	20	20
Mo	Corr.	-0.319	-.711**	1	-.544*	-.494*	-.554*	-.450*	-0.330	0.059	-0.132	-.565**
	Sig.	0.171	0.000		0.013	0.027	0.011	0.047	0.155	0.804	0.580	0.009
	N	20	20	20	20	20	20	20	20	20	20	20
Ni	Corr.	.570**	.801**	-.544*	1	.583**	.644**	.931**	.640**	0.360	.727**	.864**
	Sig.	0.009	0.000	0.013		0.007	0.002	0.000	0.002	0.118	0.000	0.000
	N	20	20	20	20	20	20	20	20	20	20	20
P	Corr.	.765**	.531*	-.494*	.583**	1	.478*	.529*	.614**	.637**	0.442	.531*
	Sig.	0.000	0.016	0.027	0.007		0.033	0.016	0.004	0.003	0.051	0.016
	N	20	20	20	20	20	20	20	20	20	20	20
Pb	Corr.	.623**	.916**	-.554*	.644**	.478*	1	.724**	0.340	0.388	.600**	.852**
	Sig.	0.003	0.000	0.011	0.002	0.033		0.000	0.143	0.091	0.005	0.000
	N	20	20	20	20	20	20	20	20	20	20	20

Table 1. – (continued)

		Ca	Fe	K	Mg	Mn	Na	Zn	Cl	SO4	HCO3
pH (field)	Corr.	-0.452	-.527*	0.196	-.586**	-0.413	-0.196	-.875**	-.536*	-.614**	.868**
	Sig.	0.052	0.020	0.421	0.008	0.079	0.420	0.000	0.018	0.005	0.000
	N	19	19	19	19	19	19	19	19	19	12
Eh	Corr.	0.393	0.403	-0.255	.525*	0.368	0.121	.840**	0.444	.543*	-.900**
	Sig.	0.096	0.087	0.292	0.021	0.121	0.621	0.000	0.057	0.016	0.000
	N	19	19	19	19	19	19	19	19	19	12
EC	Corr.	.969**	.822**	0.406	.927**	.934**	.846**	.586**	.631**	.955**	0.546
	Sig.	0.000	0.000	0.084	0.000	0.000	0.000	0.008	0.004	0.000	0.066
	N	19	19	19	19	19	19	19	19	19	12
DO	Corr.	-.540*	-.611**	-.474*	-0.368	-.516*	-.510*	-0.084	0.058	-0.447	-0.526
	Sig.	0.017	0.005	0.040	0.121	0.024	0.026	0.733	0.813	0.055	0.079
	N	19	19	19	19	19	19	19	19	19	12
As	Corr.	0.268	0.300	.675**	-0.169	0.202	0.134	-0.321	-.506*	0.057	0.418
	Sig.	0.267	0.199	0.002	0.488	0.392	0.585	0.168	0.027	0.816	0.176
	N	19	20	19	19	20	19	20	19	19	12
As (HNO3)	Corr.	0.271	0.306	.667**	-0.164	0.208	0.140	-0.318	-.501*	0.062	0.417
	Sig.	0.262	0.190	0.002	0.503	0.379	0.568	0.172	0.029	0.800	0.177
	N	19	20	19	19	20	19	20	19	19	12
As (EDTA)	Corr.	0.264	0.293	.681**	-0.176	0.195	0.128	-0.323	-.510*	0.051	0.418
	Sig.	0.274	0.209	0.001	0.471	0.409	0.601	0.165	0.026	0.835	0.176
	N	19	20	19	19	20	19	20	19	19	12
As(III)	Corr.	0.635	0.501	.732*	0.376	0.579	0.468	-0.611	-0.315	0.507	0.615
	Sig.	0.090	0.170	0.039	0.359	0.102	0.243	0.081	0.448	0.199	0.194
	N	8	9	8	8	9	8	9	8	8	6
As(V)	Corr.	0.062	0.322	0.101	-0.181	-0.058	-0.124	-0.364	-0.479	0.037	0.111
	Sig.	0.883	0.399	0.812	0.667	0.883	0.770	0.336	0.230	0.931	0.835
	N	8	9	8	8	9	8	9	8	8	6
Cd	Corr.	0.413	0.366	-0.343	.599**	0.408	0.157	.940**	.603**	.604**	-.789**
	Sig.	0.078	0.113	0.151	0.007	0.074	0.520	0.000	0.006	0.006	0.002
	N	19	20	19	19	20	19	20	19	19	12
Co	Corr.	.775**	.695**	0.312	.653**	.713**	0.446	.702**	0.345	.797**	-0.004
	Sig.	0.000	0.001	0.193	0.002	0.000	0.056	0.001	0.148	0.000	0.990
	N	19	20	19	19	20	19	20	19	19	12
Cr	Corr.	.489*	.581**	-0.214	.686**	0.433	.466*	.679**	.759**	.602**	0.005
	Sig.	0.034	0.007	0.378	0.001	0.057	0.044	0.001	0.000	0.006	0.987
	N	19	20	19	19	20	19	20	19	19	12
Cu	Corr.	0.306	0.270	-0.310	.475*	0.246	0.019	.869**	.520*	.491*	-.930**
	Sig.	0.203	0.250	0.197	0.040	0.296	0.938	0.000	0.022	0.033	0.000
	N	19	20	19	19	20	19	20	19	19	12
Mo	Corr.	-0.006	0.034	.497*	-0.324	-0.033	0.026	-.657**	-.555*	-0.194	.602*
	Sig.	0.981	0.886	0.030	0.176	0.891	0.914	0.002	0.014	0.426	0.038
	N	19	20	19	19	20	19	20	19	19	12
Ni	Corr.	.677**	.612**	0.117	.689**	.576**	.457*	.793**	.577**	.759**	-0.180
	Sig.	0.001	0.004	0.633	0.001	0.008	0.049	0.000	0.010	0.000	0.575
	N	19	20	19	19	20	19	20	19	19	12
P	Corr.	0.425	.485*	-0.206	.671**	0.435	0.364	.584**	.820**	.587**	-0.170
	Sig.	0.069	0.030	0.396	0.002	0.055	0.126	0.007	0.000	0.008	0.597
	N	19	20	19	19	20	19	20	19	19	12
Pb	Corr.	0.287	0.282	-0.213	0.442	0.201	-0.022	.800**	.486*	0.443	-.832**
	Sig.	0.233	0.229	0.382	0.058	0.395	0.928	0.000	0.035	0.057	0.001
	N	19	20	19	19	20	19	20	19	19	12

Table 2. Pearson correlation coefficients for variables Se–HCO_3 included to the statistical analyses. 2-tailed correlations significant at the 0.01 level were marked with two asterisks (**) and a gray text highlight, and 2-tailed correlations significant at the 0.05 level were marked with one asterisk (*).

		pH (field)	Eh	EC	DO	As	As (HNO3)	As (EDTA)	As(III)	As(V)	Cd	Co
Se	Corr.	-.852**	.801**	.655**	-0.257	-0.013	-0.017	-0.008	-0.348	0.057	.816**	.859**
	Sig.	0.000	0.000	0.002	0.289	0.957	0.945	0.972	0.358	0.884	0.000	0.000
	N	19	19	19	19	20	20	20	9	9	20	20
Si	Corr.	-.605**	.495*	.794**	-.525*	-0.125	-0.116	-0.135	-0.242	-0.341	.528*	.598**
	Sig.	0.006	0.031	0.000	0.021	0.599	0.626	0.570	0.530	0.369	0.017	0.005
	N	19	19	19	19	20	20	20	9	9	20	20
V	Corr.	-0.365	0.338	0.400	0.095	0.153	0.158	0.151	0.267	.779*	0.286	0.320
	Sig.	0.125	0.157	0.090	0.700	0.520	0.506	0.525	0.487	0.013	0.221	0.169
	N	19	19	19	19	20	20	20	9	9	20	20
U	Corr.	-.703**	.678**	.669**	-0.294	0.176	0.170	0.182	0.130	0.575	.670**	.752**
	Sig.	0.001	0.001	0.002	0.223	0.458	0.474	0.442	0.740	0.105	0.001	0.000
	N	19	19	19	19	20	20	20	9	9	20	20
Al	Corr.	-.944**	.912**	.571*	-0.133	-0.221	-0.222	-0.218	-0.554	-0.075	.940**	.767**
	Sig.	0.000	0.000	0.011	0.588	0.350	0.347	0.355	0.121	0.849	0.000	0.000
	N	19	19	19	19	20	20	20	9	9	20	20
Ca	Corr.	-0.452	0.393	.969**	-.540*	0.268	0.271	0.264	0.635	0.062	0.413	.775**
	Sig.	0.052	0.096	0.000	0.017	0.267	0.262	0.274	0.090	0.883	0.078	0.000
	N	19	19	19	19	19	19	19	8	8	19	19
Fe	Corr.	-.527*	0.403	.822**	-.611**	0.300	0.306	0.293	0.501	0.322	0.366	.695**
	Sig.	0.020	0.087	0.000	0.005	0.199	0.190	0.209	0.170	0.399	0.113	0.001
	N	19	19	19	19	20	20	20	9	9	20	20
K	Corr.	0.196	-0.255	0.406	-.474*	.675**	.667**	.681**	.732*	0.101	-0.343	0.312
	Sig.	0.421	0.292	0.084	0.040	0.002	0.002	0.001	0.039	0.812	0.151	0.193
	N	19	19	19	19	19	19	19	8	8	19	19
Mg	Corr.	-.586**	.525*	.927**	-0.368	-0.169	-0.164	-0.176	0.376	-0.181	.599**	.653**
	Sig.	0.008	0.021	0.000	0.121	0.488	0.503	0.471	0.359	0.667	0.007	0.002
	N	19	19	19	19	19	19	19	8	8	19	19
Mn	Corr.	-0.413	0.368	.934**	-.516*	0.202	0.208	0.195	0.579	-0.058	0.408	.713**
	Sig.	0.079	0.121	0.000	0.024	0.392	0.379	0.409	0.102	0.883	0.074	0.000
	N	19	19	19	19	20	20	20	9	9	20	20
Na	Corr.	-0.196	0.121	.846**	-.510*	0.134	0.140	0.128	0.468	-0.124	0.157	0.446
	Sig.	0.420	0.621	0.000	0.026	0.585	0.568	0.601	0.243	0.770	0.520	0.056
	N	19	19	19	19	19	19	19	8	8	19	19
Zn	Corr.	-.875**	.840**	.586**	-0.084	-0.321	-0.318	-0.323	-0.611	-0.364	.940**	.702**
	Sig.	0.000	0.000	0.008	0.733	0.168	0.172	0.165	0.081	0.336	0.000	0.001
	N	19	19	19	19	20	20	20	9	9	20	20
Cl	Corr.	-.536*	0.444	.631**	0.058	-.506*	-.501*	-.510*	-0.315	-0.479	.603**	0.345
	Sig.	0.018	0.057	0.004	0.813	0.027	0.029	0.026	0.448	0.230	0.006	0.148
	N	19	19	19	19	19	19	19	8	8	19	19
SO4	Corr.	-.614**	.543*	.955**	-0.447	0.057	0.062	0.051	0.507	0.037	.604**	.797**
	Sig.	0.005	0.016	0.000	0.055	0.816	0.800	0.835	0.199	0.931	0.006	0.000
	N	19	19	19	19	19	19	19	8	8	19	19
HCO3	Corr.	.868**	-.900**	0.546	-0.526	0.418	0.417	0.418	0.615	0.111	-.789**	-0.004
	Sig.	0.000	0.000	0.066	0.079	0.176	0.177	0.176	0.194	0.835	0.002	0.990
	N	12	12	12	12	12	12	12	6	6	12	12

Table 2. – (continued)

		Cr	Cu	Mo	Ni	P	Pb	Se	Si	V	U	Al
Se	Corr.	,584**	,811**	-,450*	,931**	,529*	,724**	1	,554*	0,429	,862**	,882**
	Sig.	0,007	0,000	0,047	0,000	0,016	0,000		0,011	0,059	0,000	0,000
	N	20	20	20	20	20	20	20	20	20	20	20
Si	Corr.	,640**	0,423	-0,330	,640**	,614**	0,340	,554*	1	0,371	,539*	,610**
	Sig.	0,002	0,063	0,155	0,002	0,004	0,143	0,011		0,107	0,014	0,004
	N	20	20	20	20	20	20	20	20	20	20	20
V	Corr.	,815**	0,259	0,059	0,360	,637**	0,388	0,429	0,371	1	,552*	0,393
	Sig.	0,000	0,270	0,804	0,118	0,003	0,091	0,059	0,107		0,012	0,087
	N	20	20	20	20	20	20	20	20	20	20	20
U	Corr.	,647**	,620**	-0,132	,727**	0,442	,600**	,862**	,539*	,552*	1	,772**
	Sig.	0,002	0,004	0,580	0,000	0,051	0,005	0,000	0,014	0,012		0,000
	N	20	20	20	20	20	20	20	20	20	20	20
Al	Corr.	,686**	,926**	-,565**	,864**	,531*	,852**	,882**	,610**	0,393	,772**	1
	Sig.	0,001	0,000	0,009	0,000	0,016	0,000	0,000	0,004	0,087	0,000	
	N	20	20	20	20	20	20	20	20	20	20	20
Ca	Corr.	,489*	0,306	-0,006	,677**	0,425	0,287	,642**	,698**	0,370	,693**	,552*
	Sig.	0,034	0,203	0,981	0,001	0,069	0,233	0,003	0,001	0,119	0,001	0,014
	N	19	19	19	19	19	19	19	19	19	19	19
Fe	Corr.	,581**	0,270	0,034	,612**	,485*	0,282	,641**	,780**	,583**	,742**	,526*
	Sig.	0,007	0,250	0,886	0,004	0,030	0,229	0,002	0,000	0,007	0,000	0,017
	N	20	20	20	20	20	20	20	20	20	20	20
K	Corr.	-0,214	-0,310	,497*	0,117	-0,206	-0,213	0,158	0,037	0,036	0,192	-0,170
	Sig.	0,378	0,197	0,030	0,633	0,396	0,382	0,519	0,881	0,883	0,432	0,488
	N	19	19	19	19	19	19	19	19	19	19	19
Mg	Corr.	,686**	,475*	-0,324	,689**	,671**	0,442	,608**	,836**	0,392	,617**	,655**
	Sig.	0,001	0,040	0,176	0,001	0,002	0,058	0,006	0,000	0,097	0,005	0,002
	N	19	19	19	19	19	19	19	19	19	19	19
Mn	Corr.	0,433	0,246	-0,033	,576**	0,435	0,201	,551*	,733**	0,280	,590**	,480*
	Sig.	0,057	0,296	0,891	0,008	0,055	0,395	0,012	0,000	0,231	0,006	0,032
	N	20	20	20	20	20	20	20	20	20	20	20
Na	Corr.	,466*	0,019	0,026	,457*	0,364	-0,022	0,339	,747**	0,274	0,354	0,279
	Sig.	0,044	0,938	0,914	0,049	0,126	0,928	0,156	0,000	0,256	0,137	0,248
	N	19	19	19	19	19	19	19	19	19	19	19
Zn	Corr.	,679**	,869**	-,657**	,793**	,584**	,800**	,817**	,663**	0,294	,664**	,932**
	Sig.	0,001	0,000	0,002	0,000	0,007	0,000	0,000	0,001	0,208	0,001	0,000
	N	20	20	20	20	20	20	20	20	20	20	20
Cl	Corr.	,759**	,520*	-,555*	,577**	,820**	,486*	0,437	,718**	0,437	0,342	,548*
	Sig.	0,000	0,022	0,014	0,010	0,000	0,035	0,061	0,001	0,062	0,151	0,015
	N	19	19	19	19	19	19	19	19	19	19	19
SO4	Corr.	,602**	,491*	-0,194	,759**	,587**	0,443	,699**	,770**	0,414	,727**	,692**
	Sig.	0,006	0,033	0,426	0,000	0,008	0,057	0,001	0,000	0,078	0,000	0,001
	N	19	19	19	19	19	19	19	19	19	19	19
HCO3	Corr.	0,005	-,930**	,602*	-0,180	-0,170	-,832**	-0,138	0,308	0,281	0,168	-,787**
	Sig.	0,987	0,000	0,038	0,575	0,597	0,001	0,670	0,331	0,376	0,602	0,002
	N	12	12	12	12	12	12	12	12	12	12	12

Table 2. – (continued)

		Ca	Fe	K	Mg	Mn	Na	Zn	Cl	SO4	HCO3
Se	Corr.	,642**	,641**	0,158	,608**	,551*	0,339	,817**	0,437	,699**	-0,138
	Sig.	0,003	0,002	0,519	0,006	0,012	0,156	0,000	0,061	0,001	0,670
	N	19	20	19	19	20	19	20	19	19	12
Si	Corr.	,698**	,780**	0,037	,836**	,733**	,747**	,663**	,718**	,770**	0,308
	Sig.	0,001	0,000	0,881	0,000	0,000	0,000	0,001	0,001	0,000	0,331
	N	19	20	19	19	20	19	20	19	19	12
V	Corr.	0,370	,583**	0,036	0,392	0,280	0,274	0,294	0,437	0,414	0,281
	Sig.	0,119	0,007	0,883	0,097	0,231	0,256	0,208	0,062	0,078	0,376
	N	19	20	19	19	20	19	20	19	19	12
U	Corr.	,693**	,742**	0,192	,617**	,590**	0,354	,664**	0,342	,727**	0,168
	Sig.	0,001	0,000	0,432	0,005	0,006	0,137	0,001	0,151	0,000	0,602
	N	19	20	19	19	20	19	20	19	19	12
Al	Corr.	,552*	,526*	-0,170	,655**	,480*	0,279	,932**	,548*	,692**	-,787**
	Sig.	0,014	0,017	0,488	0,002	0,032	0,248	0,000	0,015	0,001	0,002
	N	19	20	19	19	20	19	20	19	19	12
Ca	Corr.	1	,783**	,507*	,874**	,947**	,802**	,546*	,519*	,945**	0,493
	Sig.		0,000	0,027	0,000	0,000	0,000	0,016	0,023	0,000	0,104
	N	19	19	19	19	19	19	19	19	19	12
Fe	Corr.	,783**	1	0,406	,707**	,733**	,654**	,493*	0,422	,779**	,738**
	Sig.	0,000		0,084	0,001	0,000	0,002	0,027	0,072	0,000	0,006
	N	19	20	19	19	20	19	20	19	19	12
K	Corr.	,507*	0,406	1	0,098	0,381	0,440	-0,215	-0,204	0,252	,797**
	Sig.	0,027	0,084		0,690	0,107	0,059	0,376	0,401	0,299	0,002
	N	19	19	19	19	19	19	19	19	19	12
Mg	Corr.	,874**	,707**	0,098	1	,885**	,757**	,718**	,806**	,946**	0,277
	Sig.	0,000	0,001	0,690		0,000	0,000	0,001	0,000	0,000	0,383
	N	19	19	19	19	19	19	19	19	19	12
Mn	Corr.	,947**	,733**	0,381	,885**	1	,782**	,559*	,524*	,931**	0,439
	Sig.	0,000	0,000	0,107	0,000		0,000	0,010	0,021	0,000	0,153
	N	19	20	19	19	20	19	20	19	19	12
Na	Corr.	,802**	,654**	0,440	,757**	,782**	1	0,340	,555*	,698**	,698*
	Sig.	0,000	0,002	0,059	0,000	0,000		0,155	0,014	0,001	0,012
	N	19	19	19	19	19	19	19	19	19	12
Zn	Corr.	,546*	,493*	-0,215	,718**	,559*	0,340	1	,655**	,686**	-,592*
	Sig.	0,016	0,027	0,376	0,001	0,010	0,155		0,002	0,001	0,043
	N	19	20	19	19	20	19	20	19	19	12
Cl	Corr.	,519*	0,422	-0,204	,806**	,524*	,555*	,655**	1	,661**	-0,116
	Sig.	0,023	0,072	0,401	0,000	0,021	0,014	0,002		0,002	0,719
	N	19	19	19	19	19	19	19	19	19	12
SO4	Corr.	,945**	,779**	0,252	,946**	,931**	,698**	,686**	,661**	1	0,256
	Sig.	0,000	0,000	0,299	0,000	0,000	0,001	0,001	0,002		0,421
	N	19	19	19	19	19	19	19	19	19	12
HCO3	Corr.	0,493	,738**	,797**	0,277	0,439	,698*	-,592*	-0,116	0,256	1
	Sig.	0,104	0,006	0,002	0,383	0,153	0,012	0,043	0,719	0,421	
	N	12	12	12	12	12	12	12	12	12	12